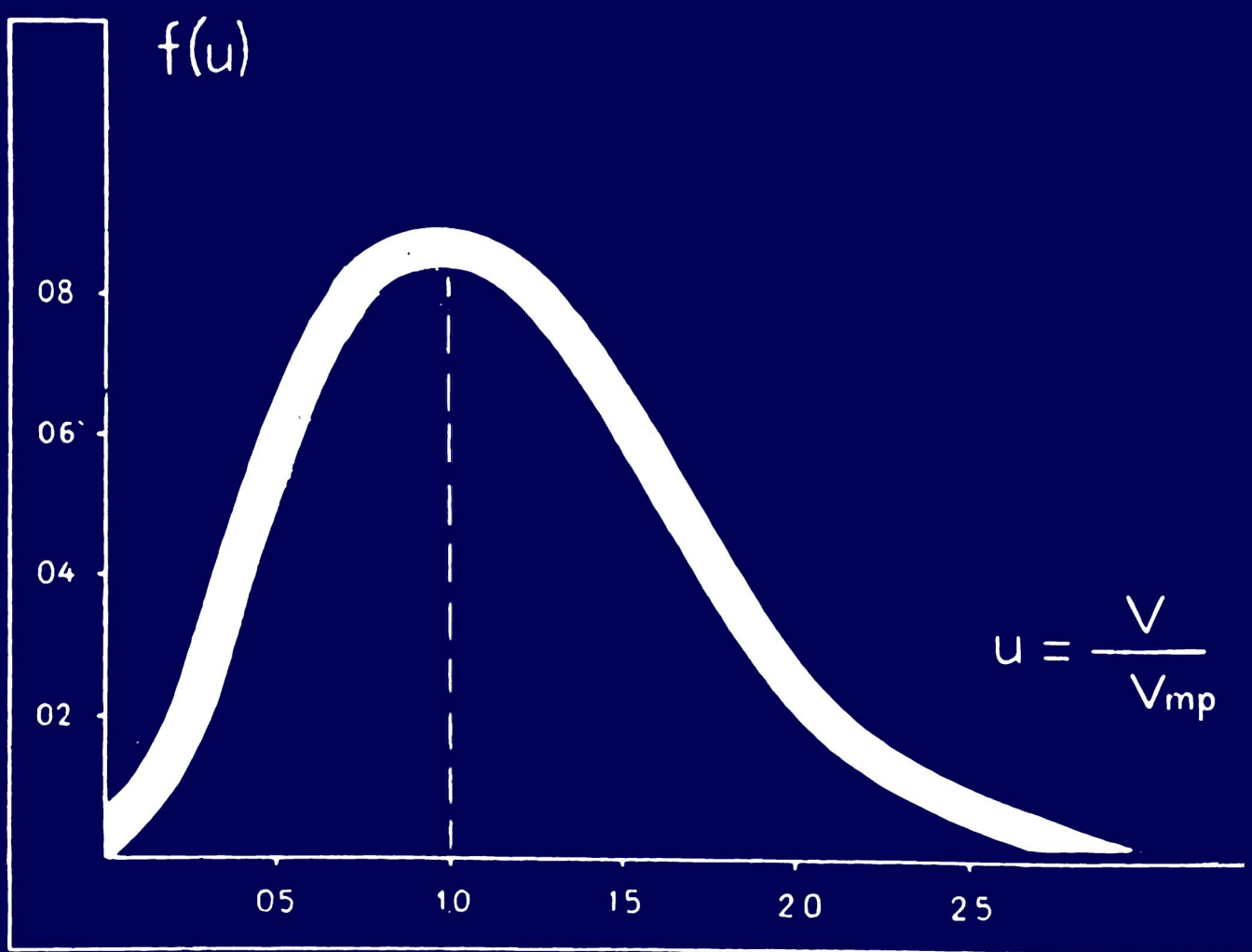
# Molecular Physics

A. KIKOIN and I. KIKOIN




MIR PUBLISHERS MOSCOW

# Molecular Physics

A. K. KIKOIN and I. K. KIKOIN

А. К. КИКОИН, И. К. КИКОИН

# МОЛЕКУЛЯРНАЯ ФИЗИКА

Издательство «Наука»
Москва

ИЗДАТЕЛЬСТВО
МИР

# Molecular Physics

A. K. KIKOIN and I. K. KIKOIN

Translated from the Russian
by G. Leib

First published 1978

Revised from the 1976 Russian edition

*На английском языке*

© Издательство «Наука», 1976

© English translation, Mir Publishers, 1978

# CONTENTS


Preface . . . . . 9

Introduction . . . . . 11

CHAPTER 1. KINETIC THEORY OF IDEAL GASES . . . . . 20

1.1. Ideal Gas . . . . . 20
1.2. Pressure of a Gas . . . . . 21
1.3. Temperature . . . . . 26
1.4. Equation of State of an Ideal Gas . . . . . 34
1.5. Ideal Gas Laws . . . . . 36
1.6. Velocities of Gas Molecules . . . . . 40
1.7. Brownian Movement . . . . . 43
1.8. Barometric Formula . . . . . 50
1.9. Boltzmann Law . . . . . 57
1.10. Concept of Probability . . . . . 57
1.11. Concept of Distribution. Distribution Function . . . . . 61
1.12. Distribution of Molecules by Velocity Components . . . . . 65
1.13. Distribution of Molecules by Velocities . . . . . 69
1.14. Mean Velocities of Molecules . . . . . 75
1.15. The Most Probable Velocity of Molecules . . . . . 78
1.16. The Maxwell Equation for Relative Velocities . . . . . 79
1.17. Velocity Distribution Law for Gas Molecules and Planets' Atmospheres . . . . . 82
1.18. Experimental Verification of Distribution Law . . . . . 84
1.19. Measuring Parameters of State . . . . . 86

CHAPTER 2. KINETIC THEORY OF HEAT. LAW OF CONSERVATION OF ENERGY. . . . . 97

2.1. Internal Energy of an Ideal Gas . . . . . 97
2.2. Quantity of Heat . . . . . 98
2.3. The Mechanical Equivalent of Heat . . . . . 99
2.4. The First Law of Thermodynamics . . . . . 100
2.5. Heat Capacity of Ideal Gases . . . . . 105
2.6. Heat Capacity of Monatomic Gases . . . . . 106

2.7. Heat Capacity of Gases and Number of Degrees of Freedom of Molecules . . . . . 109
2.8. Heat Capacity of Diatomic and Polyatomic Gases . . . . . 110
2.9. Change in State When Volume of a Gas Changes . . . . . 117
2.10. Work in Isothermal Change in Volume of an Ideal Gas . . . 118
2.11. Adiabatic Change in Volume of an Ideal Gas . . . . . 119
2.12. Work in Adiabatic Change in Volume of a Gas . . . . . 122
2.13. Polytropic Process . . . . . 124
2.14. Expansion of a Gas into a Vacuum . . . . . 126
2.15. Measurement of the Quantity of Heat and Heat Capacity. . . 127

CHAPTER 3. COLLISIONS OF MOLECULES AND TRANSPORT PHENOMENA . . . . . 132

3.1. Molecular Motion and Transport Phenomena . . . . . 132
3.2. Mean Number of Collisions in Unit Time and Mean Free Path of Molecules . . . . . 136
3.3. Effective Cross Section of a Particle and Probability . . . . . 140
3.4. Scattering of a Molecular Beam in a Gas . . . . . 142
3.5. Experimental Determination of the Free Path . . . . . 143
3.6. Diffusion in Gases . . . . . 145
3.7. Unsteady-State Diffusion . . . . . 148
3.8. Steady-State Diffusion. Calculation of the Diffusion Coefficient 151
3.9. Coefficient of Interdiffusion . . . . . 154
3.10. Thermal Diffusion . . . . . 157
3.11. Thermal Conductivity of Gases . . . . . 161
3.12. Non-Stationary Thermal Conductivity . . . . . 163
3.13. Stationary Thermal Conductivity. Calculation of the Thermal Conductivity Coefficient . . . . . 165
3.14. Viscosity of Gases (Internal Friction) . . . . . 171
3.15. Measurement of Viscosity (Viscosimetry) . . . . . 177
3.16. Relationships Between Transport Coefficients . . . . . 179

CHAPTER 4. PHYSICAL PHENOMENA IN RAREFIED GASES (A VACUUM) . . . . . 181

4.1. Heat Transfer in Gases at Low Pressures . . . . . 182
4.2. Flow of Gases at Low Pressures (Molecular Flow) . . . . . 184
4.3. Molecular Flow of a Gas in a Cylindrical Tube . . . . . 187
4.4. Molecular Flow of a Mixture of Gases. Separation of Gas Mixtures . . . . . 189
4.5. Diffusion of Gases in a Vacuum . . . . . 194
4.6. Pressure Difference Between Parts of a Gas Heated Differently (Thermal Transpiration) . . . . . 195
4.7. Elements of Vacuum Technique . . . . . 197
4.8. Measurement of Low Pressures . . . . . 202
4.9. Vacuum System . . . . . 206

CHAPTER 5. REAL GASES. VAN DER WAALS EQUATION . . . . . 208

5.1. Deviations of Gas Properties from Ideal Gas Laws . . . . . 208
5.2. Liquefaction of Gases (Condensation) . . . . . 210
5.3. Phase Transition . . . . . 216
5.4. Phase Diagrams . . . . . 218
5.5. Determination of the Critical Parameters . . . . . 219
5.6. Van der Waals Equation . . . . . 221
5.7. Van der Waals Isotherms . . . . . 226
5.8. Critical Temperature and Critical State . . . . . 229

5.9. Experimental Determination of the van der Waals Equation Constants . . . . . 233
5.10. Comparison of van der Waals Equation with Experimental Data 234
5.11. Reduced van der Waals Equation. Law of Corresponding States 236
5.12. Intermolecular Forces of Interaction in a Real Gas . . . . . 237
5.13. Heat Capacity of Real Gases . . . . . 238

CHAPTER 6. ELEMENTS OF THERMODYNAMICS . . . . . 241

6.1. Equilibrium States . . . . . 241
6.2. Reversible and Irreversible Processes . . . . . 244
6.3. Quasistatic Processes . . . . . 246
6.4. Irreversibility and Probability . . . . . 247
6.5. Mutual Conversions of Mechanical and Heat Energy . . . . . 251
6.6. The First Law of Thermodynamics . . . . . 251
6.7. Conversion of Heat into Mechanical Work . . . . . 253
6.8. The Carnot Cycle . . . . . 256
6.9. Refrigerating Machine . . . . . 262
6.10. Proof of Carnot's Theorems . . . . . 263
6.11. Free Energy . . . . . 265
6.12. Entropy . . . . . 268
6.13. Some Thermodynamic Relationships . . . . . 273
6.14. Entropy in Reversible Processes in a Closed System . . . . . 278
6.15. Entropy in Irreversible Processes in a Closed System. Law of Increase in Entropy . . . . . 279
6.16. The Second Law of Thermodynamics and the Conversion of Heat into Work . . . . . 283
6.17. Physical Meaning of Entropy. Entropy and Probability . . . 287
6.18. Entropy and Disorder . . . . . 292
6.19. The Maxwell "Demon" . . . . . 294
6.20. The Thermodynamic Temperature Scale . . . . . 295
6.21. The Third Law of Thermodynamics . . . . . 297
6.22. Negative Temperatures . . . . . 298

CHAPTER 7. PROPERTIES OF LIQUIDS . . . . . 303

7.1. Bulk Properties of Liquids . . . . . 304
7.2. Heat Capacity of Liquids . . . . . 312
7.3. Transport Processes in Liquids . . . . . 313
7.4. Phenomena on the Boundary of a Liquid . . . . . 318
7.5. Conditions of Equilibrium on the Interface Between Two Media. Contact Angle . . . . . 325
7.6. Forces Appearing on the Curved Surface of a Liquid . . . . . 329
7.7. Capillary Phenomena . . . . . 332
7.8. Some Methods of Measuring the Surface Tension . . . . . 335
7.9. Temperature Dependence of Surface Tension . . . . . 339
7.10. Evaporation and Boiling of Liquids . . . . . 339
7.11. Temperature Dependence of Saturated Vapour Pressure . . . . 343
7.12. Saturated Vapour Pressure over Curved Liquid Surface . . . . 347
7.13. Boiling of Liquids . . . . . 351
7.14. Liquid Solutions . . . . . 356
7.15. Osmotic Pressure . . . . . 361

CHAPTER 8. LOW TEMPERATURES . . . . . 363

8.1. Liquefaction of Gases . . . . . 363
8.2. Joule-Thomson Effect . . . . . 364

8.3. Adiabatic Expansion of a Gas with the Performance of External Work . . . 369
8.4. Liquefaction of Gases with the Use of the Joule-Thomson Effect (the Linde Method) . . . 372
8.5. Liquefaction of Gases by Adiabatic Expansion in Gas Expanders (the Claude Process) . . . 375
8.6. Some Properties of Liquefied Gases . . . 376
8.7. Extremely Low Temperatures . . . 378
8.8. Properties of a Substance at Low Temperatures . . . 380
8.9. Liquid Helium . . . 382

CHAPTER 9. SOLIDS . . . 392

9.1. Introduction . . . 392
9.2. Crystal Lattice . . . 395
9.3. Defects in Crystals . . . 405
9.4. Mechanical Properties of Solids. Strains . . . 408
9.5. Tensile and Compressive Strains. Shear . . . 410
9.6. Relationship Between Moduli of Elasticity . . . 413
9.7. Elastic Deformation and Thermal Expansion . . . 416
9.8. Dependence of Strain on Stress . . . 416
9.9. Mechanism of Plastic Deformation . . . 419
9.10. Dislocations in Crystals . . . 422
9.11. Transition to the Solid State . . . 426
9.12. Phase Diagram. Triple Point . . . 430
9.13. Phase Transitions of the First and Second Kinds . . . 434
9.14. Solid Helium . . . 437
9.15. Dissolution and Crystallization from a Solution . . . 439
9.16. Alloys. Fusibility Diagrams . . . 441
9.17. Zone Purification of Metals . . . 444
9.18. Experimental Determination of Melting Point . . . 447
9.19. Thermal Properties of Solids . . . 448
9.20. Measurement of Heat Capacity . . . 454
9.21. Thermal Expansion of Solids . . . 455
9.22. Thermal Conductivity . . . 458
9.23. Diffusion in Solids . . . 462

APPENDICES:

1. List of Symbols . . . 466
2. Conversion Factors for Converting SI Units to Units of Other Systems and Non-System Units . . . 468

Name Index . . . 470
Subject Index . . . 471

# PREFACE

This book has evolved from a course of lectures in molecular physics by the authors for junior students of the physics faculties of the Moscow and Sverdlovsk State Universities.

Molecular physics is a part of the course in general physics taught in the universities of the Soviet Union.

Molecular physics set out within the scope of a general course in physics should be neither a course in thermodynamics nor a course in statistical physics. But we cannot do without their elements.

It is exactly the elements of these fundamental physical theories that have been introduced into the book. In our opinion, it is not appropriate to treat the fundamentals of quantum mechanics in a book intended for junior students. We have therefore introduced only a few examples showing the limited nature of the classical notions. We consider that a course in general physics should mainly be a course in experimental physics. Much space has accordingly been devoted in the book to experimental methods used by physicists. We find it important to demonstrate to our readers the might of the means of research used in the science of physics which in our time has become the foundation of technical progress. We also consider that the introduction of physical quantities should be avoided if the ways of measuring them are not indicated.

We did everything in our power not to overload the book with mathematical calculations. But throughout the book, the essential mathematical derivations are given in detail, and at a sufficiently elementary level so as not to obscure the physical notions related to them.

We have used the SI system of units almost exclusively in the book. "Almost" because physics will hardly do completely away with the cgs system of units, just like it will continue to use such non-system units, for instance, as the electron-volt, the torr, and the atmosphere. For this reason, the reader will acquaint himself in the book with units not included in the SI system.

We hope that the present book will be helpful not only for students, but also for persons interested in physics.

*A. K. Kikoin*
*I. K. Kikoin*

# INTRODUCTION

When studying the laws controlling the motion of bodies in mechanics, we are not interested in how these bodies are constructed and what properties they have.

Bodies have a mass and definite dimensions — this was all that we knew about them. This was quite sufficient for studying motion because the result of the action of forces on a body depends only on these properties. It is obvious, however, that the dimensions and mass of bodies do not exhaust all their properties. The bodies surrounding us differ from one another not only in their dimensions and mass, but also in many other properties. And while all these other properties are of no significance in considering mechanical motion, the remaining natural phenomena are closely related to them. But the properties of bodies depend on their structure, on what parts they consist of, on what forces act between these parts, and so on. It is therefore clear that the structure of a substance is a fundamental subject of physics.

It is exactly in the present, second part of the course in physics that we shall make the first step in studying the structure of a substance. This will enable us in the following parts to delve still deeper into this most important subject of natural science that occupies the central place in modern science.

## MOLECULAR-KINETIC CONCEPTS OF A SUBSTANCE

The bodies we encounter in everyday life (especially solids and liquids) always seem to be dense or compact, i.e. completely filled with the substance forming them. Our organs of sense, which the world surrounding us directly acts on, are built so that the continuity of a substance appears to us without any doubt as its main property. A number of phenomena, however, known

already long ago, indicate that our organs of sense, which perceive bodies as compact and continuous ones, undoubtedly deceive us with respect to their true properties.

It is general knowledge, for instance, that under the action of an external force or of heating or cooling, bodies may change their volume — expand or contract. This relates to all bodies without fail, but the extent of the change may differ. It is difficult to understand such a change in the volume of bodies if we consider them to be continuous, i.e. if we consider that the substance which a body consists of fills its entire volume. But it can be explained quite easily, at least qualitatively, if we assume bodies to actually be not what they seem to us, i.e. not continuous, but to consist of an enormous number of very tiny particles, so tiny that they cannot be seen not only by the naked eye, but even through the best microscope. These particles are not in contact with one another, but have a certain distance between them. If we adopt this assumption, the change in the volume of bodies can be explained by the fact that the distances between the particles change. These most minute particles of a substance are called *molecules* (a diminutive form of the Latin word meaning mass).

The idea of the intermittent, molecular structure of a substance first appeared back in very ancient times. But for a long time it was only a conjecture of outstanding minds, a sort of hypothetic assumption. In our times, it has become a harmonious theory well supported by thousands of experiments. The multitude of direct and indirect proofs of the reality of molecules permits us to consider that the molecular concepts of the structure of a substance have been established with an authenticity on a par with that of the Copernican system.

Numerous facts make us consider that forces of repulsion and attraction act between the molecules in a substance that depend on the distance between them. One proof of this are the quite appreciable forces appearing in a solid whose volume is changed by even a small amount. It is clear that the forces of attraction between the molecules of a body prevent its stretching, and the forces of repulsion — its compression. The very existence of three states of aggregation of a substance — solid, liquid, and gaseous — indicates the existence of intermolecular forces. In the solid and liquid states, the molecules are attracted to one another to such an extent that bodies retain their volume, and solid bodies also their shape. In the gaseous state, the forces of interaction are much less. Consequently, a gas fills the entire volume placed at its disposal, no matter how big the latter is.

The last circumstance (like many others) points to another important feature of the particles of a substance. The ability of a gas to spread over the entire volume of the vessel which it is confined in shows that its molecules are in constant motion. A number of properties of gases also show that these movements of the molecules are completely chaotic. This means that there is no direction for the motion of the particles that would be favoured in comparison with any other direction (a more exact definition of the

chaotic nature of molecular motion will be given below). This chaotic motion of molecules is called *thermal motion*. The property of the molecules of a substance to be in thermal motion is not naturally a feature of only the gaseous state. The state of eternal continuous motion is equally inherent in molecules of liquids and solids, but the nature of molecular motion is somewhat different than in gases.

Thus, a substance consists of the most minute particles — molecules — that interact with one another and are in continuous chaotic motion (thermal motion).

In some states of a substance (for example in plasma, in certain crystals), negatively charged particles called *electrons* break away from molecules. The latter transform into positively charged particles — *ions*. In this case, both the ions and the electrons participate in the thermal motion.

So what are the particles which all substances are made of?

A *molecule* is the smallest particle of a substance that retains all of its chemical properties. There is no sense, for example, in speaking of half a molecule of water, and not because the molecule is indivisible, but because if it is broken up into parts, the resulting particles will no longer be particles of water.

Molecules themselves can consist of simpler particles — *atoms*. A molecule of carbon dioxide, for instance, consists of three atoms: one of carbon and two of oxygen. If the number of different species of molecules which we know is tremendous (millions), then the number of different atoms is quite small. At present, 105 different species of atoms are known, of which only 88 are encountered in nature, the remaining 17 having been obtained in the last few decades artificially. These are atoms of the so-called *chemical elements* (105 in number). The atoms of this small number of chemical elements (excluding a few inert ones) combine with one another in different ways to form molecules of the entire enormous variety of substances in the world surrounding us.

Sometimes molecules are formed of a small number of identical atoms. Such, for example, in ordinary conditions are the molecules of certain gases — oxygen ($O_2$), hydrogen ($H_2$), nitrogen ($N_2$), and others, that consist of two atoms of the relevant chemical element.

We have mentioned "ordinary conditions" here because molecules can be broken up into their constituent atoms. Such a process of decomposition of molecules is called *dissociation*. Molecules may dissociate under the action of an elevated temperature and some other external factors.

The dimensions of molecules and atoms are exceedingly small. If we imagine these particles in the form of tiny balls, then, as will be shown on a later page, their radius has a value of the order of magnitude of $10^{-8}$ cm. On the other hand, however, the number of particles is extraordinarily great. One gramme of water, for example, contains $3.3 \times 10^{22}$ molecules. The ways of experimental determination of the dimensions and number of molecules will be described in the corresponding section of the book.

The above is an outline of the fundamental concepts of the molecular-kinetic theory of the structure of matter. It is the foundation of molecular physics which the present volume is devoted to. Molecular physics studies those properties of a substance which are exactly due to the fact that it is an aggregate of a tremendous number of moving molecules.

### WHAT ATOMS ARE LIKE

We shall mainly consider such physical phenomena and processes in this book for whose description it is sufficient to know about the particles of a substance only that they are small in size and great in number. These phenomena can be explained both qualitatively and quantitatively only if we consider that atoms (which combine to form molecules) are tiny rigid elastic spheres differing, for instance, from billiard balls only in their size. This is actually not true, but for the phenomena being considered it is of no significance, just like the fact that bodies consist of separate particles instead of being solid is of no significance in studying mechanical motion.

But in some cases we shall nevertheless not be able to manage with such simple notions of atoms. We shall have to take into account the circumstance that an atom is not the limit of division of a substance, i.e. something that does not consist of anything, as the ancient atomists thought (the word "atom" means indivisible). We shall therefore briefly treat the modern ideas of the structure of atoms without going into the experimental and theoretical data that lead to these ideas. They will be dealt with in other parts of the course.

Many facts prove that atoms contain electrically charged particles. This follows first of all from the very existence of electrical and magnetic phenomena. Electrical phenomena are known to be related to a special property of bodies — an electric charge, and magnetic phenomena — to moving charges (electric currents). Since bodies are always the carriers of electrical and magnetic properties, and all bodies in the long run consist of atoms, then atoms must without fail contain moving electric charges.

At present not only the existence of moving charged particles in atoms has been reliably established, but also the "architecture" of an atom, and with the same reliability. Before setting out the modern picture of the structure of atoms, however, we must tell something about the laws that control intratomic processes. It was found when studying such processes that they cannot be completely described with the aid of conventional, so-called classical, mechanics. Moreover, it was found that our usual graphic ideas of motion cannot in general be applied to them. This is not surprising because classical mechanics was born from observations of the motion of large bodies that we can see and feel. The particles which atoms are composed of are small even in comparison with the atoms themselves. Their dimensions are of the order of magnitude of $10^{-13}$ cm, i.e. the particles distinguishable in an optical microscope are one hundred million times greater than them. The masses of these particles range from $10^{-23}$ to $10^{-27}$ g.

We shall note for comparison that the best modern balances can be used to weigh particles whose mass is from $10^{16}$ to $10^{21}$ times greater.

The entire complex of experimental data shows that atomic particles differ qualitatively from the conventional bodies considered in mechanics in the nature of their motion and in other properties.

The particles forming atoms have special, so-called quantum properties and obey the laws of *quantum mechanics*. The nature of these laws does not permit us to give an accurate and at the same time a visual description of an atomic system and its motions, i.e. such a description that would allow us to imagine its geometrical and mechanical images to which clearness is related. Therefore, we are forced to ignore strict accuracy here for the sake of clearness and give a rough picture, wittingly uncorrect, but similar to a mechanical picture of the structure of an atom.

According to this "mechanized" model, an atom is a miniature likeness of a planetary system. At its centre is a "sun" — the *atomic nucleus*, which is charged positively, and around it "planets" — negatively charged particles called *electrons* — rotate. It should be noted that an electric charge equal (in absolute value) to the charge of an electron is what we can call an "atom" of electric charge. There are no electric charges in nature that are smaller than the charge of an electron. All elementary particles without any exception, no matter what their properties and nature are (and several scores of such particles are known at present), either have no charge at all or have one that is numerically equal to or a multiple of the charge of an electron ($1.6 \times 10^{-19}$ coulomb). Hence, it follows that any electric charge, whether positive or negative, is without fail a multiple of the charge of an electron, so that the latter may serve as a unit of electric charge.

The electric forces of attraction acting between the nucleus and electrons of an atom retain the electrons around the nucleus and play the same part in the atom as the forces of universal gravitation play in "actual" planetary systems.

The atoms of different chemical elements contain different numbers of electrons. It is exactly in this that they differ from one another. But not only in this. Since in normal conditions atoms are electrically neutral, this means that no matter how many electrons an atom of an element contains, their total negative charge must numerically equal the positive charge of the atomic nucleus. Hence, atoms of different elements differ from one another not only in the number of electrons surrounding their nucleus, but also in the magnitude of the charge of the nucleus. We shall see that this difference is more important than the difference in the number of electrons.

In D. Mendeleev's periodic table, the elements are arranged in the order of increasing charge of the atomic nuclei. The atomic number $Z$ of an element in this table is a number showing how many times the positive charge of the relevant atom is greater than the charge of an electron. The absolute value of the charge of a nucleus equals, $Ze_0$, where $e_0$ is the charge

of an electron. Consequently, the atomic number of an element in Mendeleev's table directly gives us the number of electrons in its atom when it is electrically neutral.

This latter remark is very significant because an atom can contain either more or less electrons than is needed to compensate the charge of its nucleus. The matter is that one or more electrons can be detached from an atom. This does not usually require a great effort because the outer electrons further from the nucleus are comparatively weakly bound to it. The nucleus undergoes no changes when electrons are detached, but its charge is no longer compensated by the charge of the remaining electrons. The atom stops being neutral and transforms into a positively charged *ion*. On the other hand, a "surplus" electron may attach itself to a neutral atom. The latter will become a negatively charged ion because in this case too the charge of the nucleus remains unchanged.

Atoms can be ionized in various ways: by friction, heating, the illumination of bodies, impacts of fast particles, as a result of a chemical reaction, etc. All its electrons can be torn away from an atom, but in the case of many-electron atoms such complete ionization needs a much stronger action than for detaching only the outer electrons.

The particles forming atoms — electrons and nuclei — have about the same dimensions, approximately $10^{-13}$ cm, whereas the dimensions of an atom as a whole are about $10^{-8}$ cm. Hence, the particles which an atom consists of are much smaller than it itself is, just like the dimensions of the planets of the solar system and of the Sun itself are small in comparison with the radii of the planets' orbits.

As regards the mass of atomic particles, nuclei and electrons greatly differ from each other. Almost the entire mass of an atom is concentrated in its nucleus, so that only thousandths of the mass of an atom fall to the share of its electrons. For example, the mass of an iron atom nucleus is approximately $9 \times 10^{-23}$ g whereas the mass of all the 26 electrons of an iron atom is $2.3 \times 10^{-26}$ g. Hence, the mass of the nucleus is over 4000 times greater than that of the electrons.

An atomic nucleus, notwithstanding its extremely small dimensions, also has a complex structure. It consists of two kinds of particles: positively charged *protons* whose charge is numerically equal to that of an electron, and uncharged *neutrons*. Both kinds of nuclear particles are often referred to by a single name — *nucleons*. The mass of these particles is virtually the same and is about $1.7 \times 10^{-24}$ g. The number of protons in a nucleus is obviously equal to the number of electrons in the electronic shell of an atom (when it is neutral).

The number of protons in a nucleus therefore equals the atomic number of the element in Mendeleev's table, and it is exactly this circumstance that determines the chemical individuality of an atom, and not the number of electrons (we have seen that the latter can easily be changed). If, for instance, we detach from an iron atom one of its 26 electrons, we get an

ion, but it will be an ion of iron. But if we tear out one proton from the nucleus of an iron atom (this can also be done, but by absolutely different means), the result will be a radical change in the properties of the atom -- the atom of iron will transform into one of manganese.

When we indicated above that 105 different species of atoms are known at present, what we meant was that there are 105 atoms with a different number of protons, i.e. 105 different chemical elements.

As regards the neutrons, the nuclei of atoms of the same element may contain a different number of them. For example, the nucleus of an iron atom in addition to 26 protons contains 30 neutrons (this is the most widespread nucleus of iron, and ordinary iron contains 91.7% of such nuclei). But there are other nuclei of iron in which the number of neutrons (with the same 26 protons) is 28, 31, or 32. All of them are nuclei of iron, and the chemical properties of atoms having such different nuclei are absolutely the same. Only their masses differ. Such atoms whose nuclei differ from one another only in the number of neutrons in them are called *isotopes*. If we consider isotope atoms to be different atoms, then the number of different species becomes considerably greater and at present reaches 1200. It should be noted that although atoms of isotopes cannot be distinguished from one another in their chemical properties, some properties of their nuclei may cardinally differ.

Nuclear particles (protons and neutrons) are bound to one another in the nucleus by special forces of attraction — *nuclear forces*, which are neither electrical nor gravitational. They are millions of times greater in magnitude than the electric forces binding together electrons and nuclei. It is exactly the nuclear forces that are the source of so-called atomic energy. An important feature of these forces is that they act only when the distance between nucleons is very small — about the order of magnitude of the dimensions of a nucleus. With a growth in the distance, they sharply diminish. Hence, nuclear forces are often called short-range forces.

### SOME FEATURES OF QUANTUM SYSTEMS

We have already mentioned that atomic particles obey special laws — those of quantum mechanics.

The main feature of these laws which distinguishes them from the laws of classical physics is that the quantities characterizing the motion of a particle in an atom (for example the energy and pulse) can take on not any, but only quite definite values. All other conceivable values are forbidden. For instance, if we use the picture of the structure of an atom described above (which, true, has become antiquated to a considerable extent), we shall have to say that the radii of the orbits along which the electrons rotate about the nucleus can have only definite selected values, and an electron cannot be on other orbits in any conditions whatsoever.

For example in the simplest of atoms, an atom of hydrogen, its only electron in normal conditions revolves about the nucleus on an orbit with a radius of $r_0 = 5.3 \times 10^{-9}$ cm, and in no circumstances can it be closer to the nucleus. This is the smallest of the distances allowed by nature at which the electron in a hydrogen atom can be from the nucleus. A second "permissible" orbit farther from the nucleus has a radius four times greater than that of the first orbit, a third — nine times greater, a fourth — 16 times greater, etc. But the electron is "forbidden" to be anywhere between these permissible orbits.

True, an electron can pass from one of the permissible orbits to another, but such a transition must occur in a manner that is quite strange from the standpoint of conventional logics: when passing from one orbit to another, an electron cannot occupy any intermediate position. The transition must occur in a jump. The electron disappears, as it were, on one orbit and appears on another. Naturally, a particle obeying the laws of conventional mechanics cannot "jump" in this way.

As indicated above, however, the picture of an atom as a sort of miniature copy of a planetary system does not actually reflect the true structure of an atom, and it will be better to abandon this picture in general, replacing it with another one that is not so illustrative.

Definite values of the energy of an electron can be compared with the orbits of our mechanical model of an atom because when an electron moves under the action of the forces of attraction to the nucleus it has kinetic and potential energy that differs on different orbits. Consequently, instead of speaking about the orbits on which an electron rotates, we often speak of the *energy levels* which it is at. What we previously called a jump of an electron from one orbit to another is really not a transition in space, but an energy transition, i.e. a transition from a state with one energy value to a state with another value. Such transitions also occur in a jump: the energy of an electron changes directly by a definite value (a quantum), omitting all the intermediate values. Such jumps, of course, cannot be conceived in classical mechanics. When we have to use concepts of the structure of an atom, we shall use that of energy levels, and not of electron orbits.

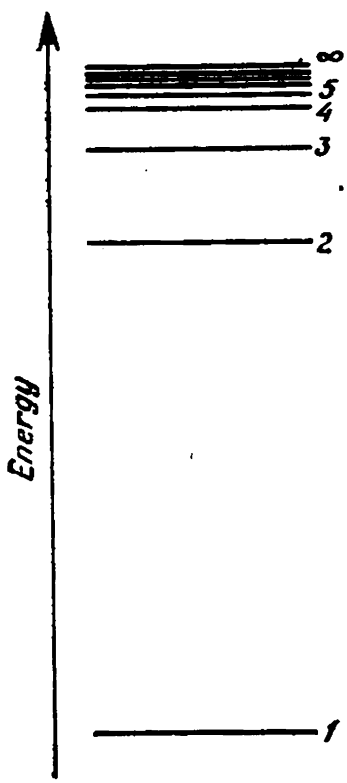


Fig. 1

Figure 1 schematically shows the energy levels of the electron in a hydrogen atom. Each of the horizontal lines conditionally corresponds to a definite value of the energy of the electron. Level *1*, the lowest energy level, corresponds to the smallest possible energy of the electron. In a hydrogen atom, it equals $2.2 \times 10^{-11}$ erg, or 13.5 electron-

volts (1 eV = $1.6 \times 10^{-12}$ erg). In normal conditions, the electron is at this level (it corresponds to the orbit closest to the nucleus in the "planetary" model). The higher levels are also permitted energy levels, but the electron can get onto them only by absorbing energy from outside. But even having absorbed energy and passed over to a higher level, which in this case is called an excitation one, the electron does not remain on it for long. In a very short time, it will return to the lower level. During this transition, it emits a portion (quantum) of light whose energy equals that of excitation. The number of permitted levels is infinitely great, but the higher the levels, the closer (from the energy viewpoint) they are to one another, merging, as it were, into an energy band.

Now we can understand the nature of the forces acting between molecules or atoms. Since atoms consist of electrically charged particles having charges of both signs, forces of attraction and forces of repulsion should act between them. But these forces are of a very intricate nature because every atom contains many charged particles.

CHAPTER 1

# KINETIC THEORY OF IDEAL GASES

## 1.1. IDEAL GAS

In the greater portion of the phenomena which this book is devoted to, there is no need not only to take into account the quantum nature of intratomic processes, but even to give attention to the very fact of the existence of a structure in atoms. Our task is to study systems consisting of a great number of molecules which are considered as being bodies having a small size and mass.

The theoretical investigation of such molecular systems is naturally connected with great difficulties because for this purpose all the forces acting on each molecule from all the others must be taken into account. If we assume that the movements of the molecules are purely mechanical and obey the laws of mechanics, then for a complete description of a molecular system we would apparently have to solve the problem, relating to mechanics, on the motion of all the molecules under the action of the given forces. This means that we would have to write down and solve as many equations of motion as there are molecules in a given system (more exactly, the number of equations should be three times greater because the position of a molecule is determined by three coordinates, i.e. every molecule has three degrees of freedom). If we take into account that, for example, 1 $cm^3$ of a gas in ordinary conditions contains $2.7 \times 10^{19}$ molecules, it becomes clear that it is not only impossible to solve, but even to write down such an enormous number of equations.

But it is exactly the immensity of the number of molecules that makes it unnecessary to consider the motion of each of them separately. With such a great number of particles, we may limit ourselves to a knowledge of only the mean values of the quantities characterizing their motion: their mean velocity, mean energy, etc. We shall follow this procedure in studying molecular systems.

Of the three states of aggregation in which a substance may be, the gaseous state is the simplest because in this case the forces acting between the

molecules are very small, and in definite conditions they may be disregarded. This is the reason why we shall begin our treatment of molecular physics with a consideration of the properties of gases. We shall first assume that the intermolecular forces in them are completely absent instead of being small. For simplicity, we shall also ignore the dimensions of the molecules, i.e. consider them to be material points. With such assumptions, the molecules of a gas should be considered absolutely free. This means that they move rectilinearly and uniformly, as bodies always do if no forces act on them. Hence, each molecule behaves as if there are no other molecules in the vessel.

Later on, when dealing with real gases, we shall eliminate these arbitrary assumptions although they are justified by the fact that in definite conditions such idealization does not carry us too far away from actual conditions.

A gas having the same properties as an aggregate of non-interacting material points is called an *ideal gas*. Treatment of the kinetic theory of ideal gases will be our first task.

## 1.2. PRESSURE OF A GAS

The picture of the movements of molecules in a gas will be incomplete if we do not consider the collisions of the molecules with the surface of any body in the gas, in particular with the walls of the vessel containing the gas and with one another.

Indeed, in performing chaotic movements, the molecules from time to time approach the walls of the vessel or the surface of other bodies to sufficiently small distances. In exactly the same way, the molecules may come sufficiently close to one another. In this case, forces of interaction appear between the molecules of the gas or between a molecule of the gas and molecules of the substance of the wall that decrease very rapidly with the distance. These forces cause the molecules of the gas to change the direction of their motion. This process (a change in direction) is called a *collision*.

Collisions of molecules with one another play a very great part in the behaviour of a gas. And we shall study them later in greater detail. Here it is important to take account of the collisions of molecules with the walls of the vessel or with any other surface in contact with the gas. It is exactly the interaction between the molecules of the gas and the walls that determines the force exerted on the walls by the gas and, naturally, the equal and oppositely directed force exerted on the gas by the walls. It is quite obvious that the force exerted by a gas on a wall is the greater, the larger is the area of the surface of the wall. To avoid using a quantity that depends on such a random factor as the dimensions of the wall, it is customary practice to characterize the action of a gas on a wall not by the force, but

by the *pressure p*, i.e. the force $F$ related to a unit of the area $A$ of the surface of the wall perpendicular to this force:

$$p = \frac{F}{A}$$

The ability of a gas to exert a pressure on the walls of the vessel containing it is one of its main properties. It is most frequently the pressure of a gas that discloses its presence. Therefore, the magnitude of the pressure is one of the main characteristics of a gas.

The pressure of a gas on the walls of a vessel, as Daniel Bernoulli assumed back in the 18th century, is the result of innumerable collisions of its molecules with the walls. These impacts of the molecules against the walls result in certain displacements of the particles of the wall material and, consequently, in deformation of the walls. The deformed wall, in turn, acts on the gas with an elastic force that is directed at each point perpendicularly to the wall. This force is equal in absolute value and opposite in direction to the force with which the gas acts on the wall.

Although the forces of interaction of each separate molecule with the molecules of the wall upon a collision are unknown, the laws of mechanics nevertheless allow us to find the mean force appearing as a result of the joint action of all the molecules of the gas, i.e. to find the pressure of the gas.

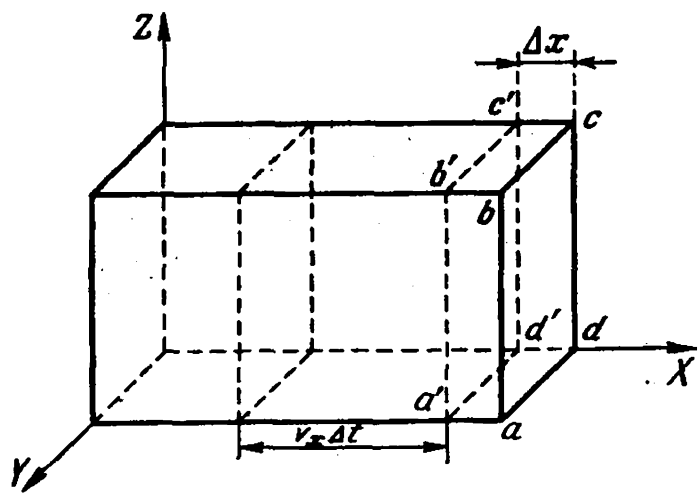



Fig. 2

Assume that a gas is confined in a vessel having the shape of a parallelepiped (Fig. 2) and that the gas is in the state of equilibrium. In the given case, this means that the gas *as a whole* is at rest relative to the walls of the vessel. The number of molecules travelling in any arbitrary direction is equal on an average to the number of molecules travelling in the opposite direction.

Let us calculate the pressure of the gas on one of the walls of the vessel, for example on right-hand side wall *abcd*. We direct the coordinate axis

$X$ along the edge of the parallelepiped perpendicular to wall *abcd* as shown in Fig. 2. Regardless of the directions of the velocities $v$ of the molecules, we shall be interested only in the projections $v_x$ of the velocities onto the $X$-axis: the molecules will travel with the velocity $v_x$ toward wall *abcd*.

Let us mentally separate a layer of gas with a thickness of $\Delta x$ adjoining the chosen wall. The elastic force $\boldsymbol{F}$ will act on it from the side of the deformed wall. The gas will act on the wall with a force that is the same in absolute value. According to Newton's second law, the impulse of the force, $\boldsymbol{F}\Delta t$ (where $\Delta t$ is a certain arbitrary interval of time) is equal to the change in the impulse of the gas in our layer. But the gas is in a state of equilibrium so that the layer receives no growth in the impulse in the direction of the impulse of the force (opposite to the positive direction of the $X$-axis). This occurs because owing to molecular movements, the separated layer receives an impulse of the opposite direction and, naturally, having the same absolute value. It is simple to calculate.

Upon the chaotic movements of the gas molecules, a certain number of molecules will enter our layer from left to right during the time $\Delta t$, and the same number of molecules will emerge from it in the reverse direction, from right to left. The entering molecules bring along a definite impulse. The emerging molecules carry the same impulse of the opposite sign, so that the total impulse received by the layer equals the algebraic sum of the impulses of the entering and emerging molecules.

Let us find the number of molecules entering our layer from the left during the time $\Delta t$.

During this time, boundary $a'b'c'd'$ can be approached from the left by the molecules that are at a distance from it not exceeding $v_x \Delta t$. All of them are confined in the volume of a parallelepiped with a base area of $A$ (this is the area of the wall being considered) and a length of $v_x \Delta t$, i.e. in the volume $Av_x \Delta t$. If a unit of volume of the vessel contains $n$ molecules, then the volume of the layer contains $nAv_x \Delta t$ molecules. But only half of them are travelling from left to right and will enter the layer. The other half are travelling *from* it and will not enter the layer. Hence, during the time $\Delta t$, the layer will be entered from *left to right* by $\frac{1}{2} nAv_x \Delta t$ molecules. Each of them has an impulse or momentum of $mv_x$ (where $m$ is the mass of a molecule), and the total impulse which they bring into the layer is

$$\frac{1}{2} nmv_x^2 A \, \Delta t$$

During the same time, an identical number of molecules having the same total impulse, but of the opposite sign, leave the layer travelling from *right to left*. Thus, owing to the layer being entered by molecules having

a positive impulse and left by molecules having a negative impulse, the total change in the impulse in the layer is

$$\frac{1}{2} nmv_x^2 A\,\Delta t - \left(-\frac{1}{2} nmv_x^2 A\,\Delta t\right) = nmv_x^2 A\,\Delta t$$

It is exactly this change in the impulse of the layer that will compensate for the change that should have occurred under the action of the impulse of force $F\,\Delta t$. We can therefore write that

$$F\,\Delta t = nmv_x^2 A\,\Delta t$$

Dividing both sides of this equation by $A\,\Delta t$, we get

$$\frac{F}{A} = p = nmv_x^2 \tag{1.1}$$

Up to now, we tacitly assumed that for all the molecules of a gas the projections of the velocity $v_x$ are the same. In actual conditions, this is naturally not how matters are. Both the velocities of different molecules $v$ and the projections $v_x$ on the $X$-axis are different. The difference in the velocities of gas molecules in equilibrium conditions will be considered in detail in Sec. 1.12. Meanwhile, we shall take into account the difference in the velocities of the molecules and in their projections on the axes of coordinates by substituting the *mean* value $\overline{v_x^2}$ for the quantity $v_x^2$ in Eq. (1.1). Hence, the formula for the pressure of a gas becomes

$$p = nm\overline{v_x^2} \tag{1.2}$$

For the velocity $v$ of each molecule, we can write

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

hence

$$\overline{v^2} = \overline{v_x^2 + v_y^2 + v_z^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \tag{1.3}$$

(the latter equation signifies that the sequence of conducting the operations of determining the mean values and summation may be changed). Owing to the complete disorder of molecular movements, we can assume that the mean values of the squares of the velocity projections on the three axes of coordinates equal one another, i.e.

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

And this means, with a view to Eq. (1.3), that

$$\overline{v_x^2} = \frac{\overline{v^2}}{3}$$

Using this expression in Eq. (1.2), we get

$$p = \frac{1}{3} nm\overline{v^2}$$

or, multiplying and dividing the right-hand side of this equation by two, we have

$$p = \frac{2}{3} n \frac{\overline{mv^2}}{2} \tag{1.4}$$

The above simple reasoning holds for any wall of a vessel and for any area that can be mentally placed in a gas. We shall always get the result expressed by Eq. (1.4) for the pressure of a gas. The quantity $\overline{mv^2}/2$ in Eq. (1.4) is the mean kinetic energy of one molecule of a gas. Consequently, *the pressure of a gas equals two-thirds of the mean kinetic energy of the molecules contained in a unit of its volume.*

This is one of the most important conclusions of the kinetic theory of an ideal gas. Equation (1.4) establishes a relationship between molecular quantities, i.e. quantities relating to a separate molecule, and the value of the pressure characterizing a gas as a whole — a macroscopic quantity directly measured in experiments. Equation (1.4) is sometimes called the fundamental equation of the kinetic theory of ideal gases.

It is important to stress that the pressure of a gas is determined by the *mean* kinetic energy of its molecules. This means that the pressure of a gas is a quantity integrally connected with the fact that the gas consists of a great number of molecules. Therefore, there is no sense in speaking, for example, of the pressure created by one or a few molecules. Concepts having sense only for a system containing very many particles are said to have a *statistical* nature.

It must be noted here that the *mean value of the square of the velocity* $\overline{v^2}$ in Eq. (1.4) should be distinguished from the *square of the mean value of the velocity* $\overline{v}^2$. The square root of $\overline{v^2}$ equals the mean velocity $\overline{v}$, but the square root of $\overline{v^2}$ does not equal $\overline{v}$.

The quantity $\sqrt{\overline{v^2}} = \overline{v}$ (and not $\overline{v}$) is called the *mean square* (or *effective*) *velocity* of molecules. If the motion of molecules is chaotic, their mean square velocity is about 9% greater than their mean velocity.

**Units of Pressure.** In the SI system, the unit of pressure is the pressure at which a force of 1 newton acts on 1 $m^2$ of a surface normal to it. This unit is called the *pascal* (Pa):

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

Owing to the small value of this unit, it is recommended to use a unit that is $10^5$ times greater called the *bar*:

$$1 \text{ bar} = 10^5 \text{ Pa}$$

In the cgs system, the pressure is measured in dyn/cm²:

$$1 \text{ dyn/cm}^2 = 0.1 \text{ Pa}$$

In engineering, a unit of pressure called the *technical atmosphere* (at) and equal to 1 kgf/cm² is in great favour. This unit differs from the bar by only 2%:

$$1 \text{ at} = 1 \text{ kgf/cm}^2 = 98\,066.5 \text{ Pa} \approx 0.98 \text{ bar}$$

Sometimes physical atmospheres (atm) are used to measure pressure. A *physical atmosphere* equals the pressure of a column of mercury 76 cm (or 0.76 m) high. Considering the density of mercury equal to 13.5951 g/cm³ (13 595.1 kg/m³) and the acceleration of free fall equal to 9.806 65 m/s², we get

$$1 \text{ atm} = 0.76 \times 13\,595.1 \times 9.806\,65 = 101\,325 \text{ Pa} =$$

$$= 1.013\,25 \times 10^6 \text{ dyn/cm}^2 \ (\approx 1.01 \text{ bar})$$

In the region of low pressures, the pressure unit called the *torr* (millimetre of mercury) is used:

$$1 \text{ torr} = 1 \text{ mm Hg} = \frac{1}{760} \text{ atm} = 133.322 \text{ Pa} \approx 1.33 \times 10^3 \text{ dyn/cm}^2$$

When solving problems, we must remember that all the units given above are non-system ones except for the pascal (SI system) and the dyn/cm² (cgs system).

## 1.3. TEMPERATURE

From Eq. (1.4)

$$p = \frac{2}{3} n \frac{\overline{mv^2}}{2}$$

it follows that the pressure of an ideal gas is proportional to its density (the latter is determined by the number of molecules $n$ in a unit of volume of the gas) and the mean kinetic energy of translational motion of the molecules. When $n$ is constant and, consequently, the volume of the gas $V$ is constant ($n = N/V$, where $N$ is the number of molecules in the vessel), the pressure of a gas depends only on the mean kinetic energy of the molecules.

It is known from experience that at constant volume, the pressure of a gas can be changed only in one way — by heating or cooling it. Heating causes the pressure of a gas to grow, and cooling causes it to decrease. A heated or a cooled gas, like any body, is characterized by its *temperature* — a special quantity that has been in use for a long time in science, engineering,

and everyday life. Hence, there should be a relationship between the temperature and the mean kinetic energy of molecules.

Before finding this relationship, let us see what temperature is as a physical quantity.

In our everyday life, temperature is a quantity for us that distinguishes "hot" from "cold". And our first notions of temperature appeared from our feeling heat and cold. We can use these familiar sensations to determine the main feature of temperature as a physical quantity.

Let us take three vessels. We pour hot water into one of them, cold water into the second, and a mixture of the hot and cold water into the third. Now we immerse one hand, for example the right one, into the vessel with hot water, and the left hand into the vessel with cold water. After keeping our hands for some time in these vessels, we transfer them to the third vessel. What will our feelings tell us about the water in this vessel? It will seem to the right hand that the water in it is cold, and to the left hand that it is warm. But this "contradiction" will vanish if we keep both hands in the third vessel for a longer time. After a certain time has elapsed, both hands will begin to feel absolutely the same sensations, which correspond to the temperature of the water in the third vessel.

The matter is that our hands, after being in the vessels with the hot and cold water, had different temperatures, differing both from each other and from the temperature in the third vessel. And some time is needed for the temperature of each of our hands to become equal to the temperature of the water they are immersed into. After this time, the hands acquire the same temperature. The feelings will also be the same. It is necessary, as is said, for *thermal equilibrium* to set in in the system of bodies "right hand-left hand-water".

This simple experiment shows that temperature is a quantity characterizing the state of thermal equilibrium. Bodies in the state of thermal equilibrium have the same temperature. And, conversely, bodies having the same temperature are in thermal equilibrium with one another. *And if two bodies are in thermal equilibrium with a third body, then both bodies are in thermal equilibrium with each other.* This important statement is one of the main laws of nature. And the very possibility of measuring temperature is based on it. In the experiment described above, for instance, we spoke of thermal equilibrium of both hands after each of them was found to be in thermal equilibrium with the water.

If a body or a system of bodies is not in a state of thermal equilibrium, and if the system is isolated (it does not interact with other bodies), then after a certain time the state of thermal equilibrium will set in by itself. The state of thermal equilibrium is the state which any isolated system passes into. After such a state is reached, it will no longer change, and no macroscopic changes will occur in the system. The equality of the temperatures of all the parts of a body or all the bodies of a system is one of the indications of the state of thermal equilibrium. It is known that in the

process of the setting in of thermal equilibrium, i.e. when the temperatures of two bodies become equalized, heat is transferred from one body to the other. Consequently, from the experimental viewpoint, the temperature of a body is a quantity that determines whether it will transfer heat to another body having a different temperature or receive heat from it.

Temperature occupies a special place in the array of physical quantities. This is not surprising if we take into account that in the era when this quantity appeared in science, nobody knew what internal processes in a substance cause the feeling of heat and cold.

The distinctive nature of temperature as a physical quantity consists first of all in that in contrast to many other quantities it *is not additive.* This means that if we mentally divide a body into parts, the temperature of the entire body will not equal the sum of the temperatures of its parts. In this feature, temperature differs from such quantities, for instance, as length, volume, and mass, whose values for an entire body are the sums of the relevant values for its parts.

The result is that the temperature of a body cannot be measured directly like length or mass, i.e. by the method of comparing with a standard. If we can say about a rod that its length is so many times greater than that of another rod, the question of how many times one temperature is contained in another is deprived of any meaning.

The fact that properties of a body change with changing temperature underlies the ways of measuring temperature that have been in use for a long time. Consequently, what is measured are the quantities characterizing these properties. Hence, for creating an instrument measuring the temperature, i.e. a *thermometer*, an appropriate substance is selected (a *thermometric substance*) and an appropriate quantity characterizing a property of this substance (a *thermometric quantity*). The selection of the substance and the quantity is arbitrary. In domestic thermometers, for example, the thermometric substance is mercury, and the length of the column of mercury is the thermometric quantity.

To be able to express the temperature using definite numerical values, we must also choose a relationship of the thermometric quantity to the temperature. The selection of this relationship is also arbitrary — as long as we have no thermometer, we cannot establish this relationship experimentally! When using a mercury thermometer, for example, we choose a linear dependence of the length of the mercury column (the volume of the mercury) on the temperature.

It remains to establish the unit of temperature — the *degree* (although in principle it could be expressed in the same units in which the thermometric quantity is measured, for instance in centimetres in a mercury thermometer!). The value of a degree is also selected arbitrarily (like the thermometric substance, the thermometric quantity, and the form of the function relating the thermometric quantity to the temperature). The value of a degree is established as follows. Two temperatures are chosen,

again arbitrarily (they are called *datum* or *reference points*) — usually they are the melting point of ice and the boiling point of water at atmospheric pressure — and the temperature interval between them is divided into a number (also arbitrary) of equal parts called degrees. A definite numerical value is assigned to one of the two reference points. Thus we determine the value of the second temperature and of any intermediate one, i.e. we obtain a *temperature scale*. It is obvious that we can use this procedure to obtain a countless number of different thermometers and temperature scales.

Modern thermometry is based on the *ideal gas scale*, established with the aid of a *gas thermometer*. In principle, the latter is a closed vessel filled with an ideal gas and provided with a pressure gauge for measuring the pressure of the gas. Hence, the thermometric substance in such a thermometer is the ideal gas, and the thermometric quantity — the pressure of the gas at constant volume. The dependence of the pressure on the temperature is *assumed* (we must stress the word assumed!) to be linear. This assumption results in the ratio of the pressures at the boiling point of water ($p_b$) and the melting point of ice ($p_0$) being equal to the ratio of these temperatures themselves:

$$\frac{p_b}{p_0} = \frac{T_b}{T_0}$$

The ratio $p_b/p_0$ can be easily determined experimentally. A multitude of measurements have shown that

$$\frac{p_b}{p_0} = 1.3661$$

Hence, the ratio of the temperatures

$$\frac{T_b}{T_0} = 1.3661$$

The value of a degree is chosen by dividing the difference $T_b - T_0$ into 100 parts:

$$T_b - T_0 = 100$$

It follows from the last two equations that the melting point of ice $T_0$ according to the scale we have chosen is 273.15 degrees, and the boiling point of water $T_b$ is 373.15 degrees. To measure the temperature of a body with the aid of a gas thermometer, we must bring the body in contact with it and, after waiting for equilibrium to set in, measure the pressure $p$ of the gas in the thermometer. The temperature $T$ of the body will therefore be determined by the equation

$$T = \frac{273.15}{p_0} p$$

where $p_0$ is the pressure of the gas in the thermometer placed in melting ice.

Gas thermometers are used very seldom in practice. They have been assigned a more responsible part — all thermometers in use are graduated according to them.

The temperature equal to zero in our scale is obviously the temperature at which the pressure of an ideal gas would equal zero. (This does not mean that an ideal gas can actually be cooled to such an extent that its pressure will become equal to zero.) If at the zero of the temperature scale a thermometric quantity becomes equal to zero, such a scale is called *absolute*, and the temperature determined according to such a scale is called the *absolute temperature*. The gas thermometer scale we have described is absolute. It is often also called the *Kelvin scale*, and the unit of temperature in this scale — the *kelvin* (K).

In engineering and everyday life, a temperature scale is often used which differs from the one described above in that the melting point of ice is taken equal to zero (with the same value of a degree). This scale is called the *Celsius scale*. The temperature $t$ read off on this scale is related to the absolute temperature $T$ by the expression

$$t = T - 273.15$$

We shall use the Kelvin scale in the following.

It follows from the above that temperature characterizes the thermal equilibrium of bodies: when passing to a state of equilibrium, the temperatures of bodies level out, and in the state of equilibrium the temperature of all the parts of a body or a system of bodies is the same. The procedure itself of measuring temperature is connected with such equilibrium. To measure the value of a thermometric quantity at the melting point of ice and the boiling point of water, the thermometer must be brought into a state of equilibrium with the melting ice and the boiling water; and to measure the temperature of a body, it is necessary to ensure the possibility of thermal equilibrium setting in between the thermometer and the body. And only when such equilibrium has been reached may we consider that the temperature of the body equals the temperature shown by the thermometer.

Thus, the temperature is what levels out when equilibrium sets in in a system. But the very concept of levelling out means that something is transferred from one part of the system to another. Equation (1.4) which we obtained for the pressure of an ideal gas will permit us to understand what this "something" is.

Imagine an isolated cylinder containing an ideal gas in which thermal equilibrium has already set in, so that the temperature at all parts of the volume of the gas is the same. Assume that without violating equilibrium, a movable piston is placed in the cylinder that divides the volume of

the gas into two parts (Fig. 3*a*). In conditions of equilibrium, the piston will be at rest. This means that in equilibrium not only the temperatures but also the pressures at both sides of the piston are the same. According to Eq. (1.4), the quantities $n(m\overline{v^2}/2)$ are also the same:

$$\left(n\frac{m\overline{v^2}}{2}\right)_{\text{left}} = \left(n\frac{m\overline{v^2}}{2}\right)_{\text{right}}$$

Let us now temporarily violate the isolation of our cylinder with gas and heat one of its parts, for example the one to the left of the piston, after which we shall again restore the isolation. Now the gas in the cylinder is not in equilibrium — the temperature $T_1$ in the left-hand part is higher than in the right-hand one (Fig. 3*b*). But the gas is isolated, and the transition to a state of equilibrium will begin spontaneously. The piston will be seen to move from left to right. This means that *work* is being performed, and, consequently, that *energy* is transmitted from the gas in the left-hand part to the gas in the right-hand one through the piston. Hence, what is transmitted in the process of setting in of thermal equilibrium is *energy*. After some time, the motion of the piston will stop. But it will stop after a number of oscillations. And it will stop at exactly the same place where it had been before the left-hand part of the cylinder was heated. A state of equilibrium again sets in in the cylinder with the gas. But now, of course, the temperature of the gas and its pressure are higher than before heating.

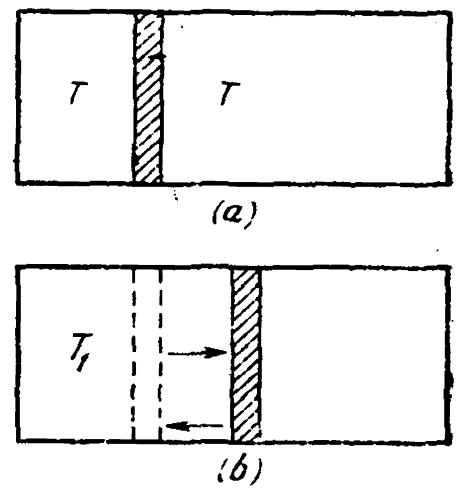


Fig. 3

Since the piston stopped at its previous location, the concentration $n$ of the molecules (i.e. the number of molecules in a unit volume) remained the same. This means that as a result of heating of the gas only the mean kinetic energy of its molecules changed. Levelling out of the temperature, therefore, means levelling out of the values of the mean kinetic energy of the molecules at both sides of the piston. In transition to equilibrium, energy is transmitted from one part of the gas to the other. What is levelled out, however, is not the energy of the entire gas as a whole, but the mean kinetic energy related to one molecule. It is exactly the mean kinetic energy of a molecule that behaves like the temperature.

These two quantities are also similar in that the mean kinetic energy, like the temperature, is not an additive quantity. It is the same for the entire gas and for any part of it (containing a sufficiently great number of molecules). The energy of the entire gas is naturally an additive quantity — it is the sum of the energies of its parts.

Our reasoning should not be thought to relate only to the case when the gas in the cylinder is divided into two parts by a piston. Even without the piston, the molecules upon collisions between them would exchange energy, and it would be transmitted from the warmer part to the cooler one, as a result of which the mean kinetic energies of the molecules would level out. The piston only makes the transfer of energy appear visible because its motion is connected with the doing of work.

The above simple but not very strict reasoning shows that the quantity known for a long time under the name of temperature is really the mean kinetic energy of the translational motion of molecules. Matters are not changed by the fact that we obtained this result for an ideal gas. There are no grounds to consider that it does not also relate to liquids and solids.

When applied to an ideal gas, it is more convenient to consider that the temperature equals two-thirds of the mean kinetic energy of the molecules because this simplifies the form of Eq. (1.4) for the pressure of a gas. Letting $\Theta$ stand for the temperature determined in this way, we can write:

$$\frac{2}{3}\frac{m\overline{v^2}}{2} = \Theta$$

Hence, Eq. (1.4) acquires the simple form

$$p = n\Theta$$

With such a definition of temperature, it should obviously be measured in units of energy (in the SI system — in joules, in the cgs system — in ergs). In practice, however, it is not convenient to use such units for temperature. Even such a small unit of energy as the erg is too great to serve as a temperature unit. If it were used, the temperatures usually encountered would be expressed in negligibly small numbers. For instance, the melting point of ice would be $5.65 \times 10^{-14}$ erg. In addition, it would also be very difficult to measure temperature in ergs.

For this reason, and also because the magnitude of the temperature had been used long before molecular-kinetic notions developed, which explain the true meaning of temperature, it is nevertheless measured in the old units — degrees (kelvins), notwithstanding the conditional nature of this unit.

But if we measure temperature in kelvins, we must introduce the corresponding factor for converting energy units to kelvins. It is conventionally denoted by $k$. Hence, the relationship between the temperature $T$ measured in kelvins and the mean kinetic energy will be

$$\frac{2}{3}\frac{m\overline{v^2}}{2} = kT$$

whence

$$\frac{m\overline{v^2}}{2} = \frac{3}{2}kT \qquad (1.5)$$

It should be remembered that Eq. (1.5) relates to a molecule which we have agreed to consider similar to a point. Its kinetic energy is that of *translational* motion whose velocity can be resolved into three components. Owing to the chaotic nature of molecular motion, we can assume that the energy of a molecule is uniformly distributed among all three velocity components, so that the energy $kT/2$ falls to each of them.

The factor $k$ expressing the relationship between a unit of energy and the unit of temperature, the kelvin, is called the *Boltzmann constant*. It is clear that its numerical value must be established experimentally. Owing to the special importance of this constant, it was determined in many ways. The value of this constant considered at present to be the most accurate is

$$k = 1.380\,662 \times 10^{-23}\ \text{J/K}$$

in the SI system, and

$$k = 1.380\,662 \times 10^{-16}\ \text{erg/K}$$

in the cgs system.

It follows from Eq. (1.5) that when the temperature equals zero the mean kinetic energy of the chaotic motion of the molecules also equals zero, i.e. the chaotic motion of the molecules stops. This is exactly the absolute zero of the temperature scale mentioned on a previous page.

It also follows from Eq. (1.5) that there can be no negative temperatures because kinetic energy is essentially a positive quantity. Nevertheless, we shall show in Chap. 6 that the concept of negative temperatures can be formally introduced for definite systems. True, it will be impossible to say that these are temperatures below absolute zero and that they relate to the equilibrium state of a system.

Since temperature is determined by the *mean* energy of motion of molecules, then, like pressure, it is a statistical quantity. We cannot speak about the "temperature" of one or a few molecules, about "hot" or "cold" molecules. There is no sense, for example, to talk about the temperature of a gas in outer space where the number of molecules in a unit of volume is so small that they do not form a gas in the usual meaning of the word, and we cannot speak of the mean energy of motion of the molecules.

The values of the energy connected with the chaotic motion of gas particles are very low. It can be seen from Eq. (1.5) and from the value of the Boltzmann constant given above that an energy equal to $1.38 \times 10^{-23}$ J corresponds to a temperature of 1 K. At the lowest temperature reached at present (of the order of magnitude of $10^{-6}$ K) the mean energy of molecules is about $10^{-29}$ J. A negligible energy of particles of about $10^{-15}$ J corresponds even to the highest artificially obtained temperature of about 100 million kelvins developed upon the explosion of an atomic bomb.

Since temperature plays a very important part in physics and engineering, it is included together with length, mass, and time among the basic quantities of the SI system, and the unit of temperature — the kelvin — is one of

the basic units of this system (the dimension of temperature is denoted by the letter Θ).

In the SI system, the unit of temperature (the kelvin) is established not on the basis of the temperature interval between the melting point of ice and the boiling point of water, but on the basis of the interval between absolute zero and the triple point of water. The latter is the temperature at which water, water vapour, and ice are in equilibrium (see Sec. 9.12). The value of 273.16 K (exactly) is assigned to the triple point of water.

Thus, *one kelvin equals 1/273.16th of the temperature interval from the absolute zero of temperature to the triple point of water.*

Since the triple point of water is 0.01 °C, the magnitude of a degree of the Celsius scale and a kelvin is the same, and, therefore, temperature intervals measured using either of these scales will be identical.

## 1.4. EQUATION OF STATE OF AN IDEAL GAS

The molecular-kinetic notions developed above and the equations obtained on their basis permit us to find the relationships between the quantities that determine the state of a gas. These quantities are the pressure $p$ under which the gas is, its temperature $T$, and the volume $V$ occupied by a definite mass of the gas. They are called the *parameters of state.*

These three quantities are not independent. Each of them is a function of the other two. An equation relating all three quantities — the pressure, volume, and temperature of a gas for its given mass, is called an *equation of state* and in the general form can be written as follows:

$$p = f(V, T)$$

This means that the state of a gas is determined by only two parameters (for instance pressure and volume, pressure and temperature, or, finally, volume and temperature), the third parameter being unambiguously determined by the other two. If an equation of state is known in an explicit form, then any parameter can be calculated if we know the other two.

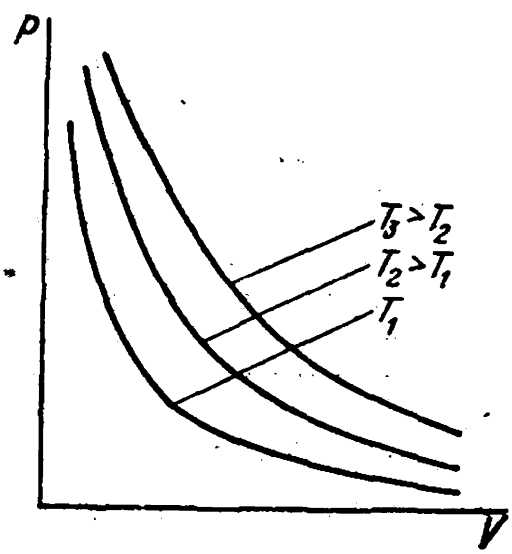



Fig. 4

To study different processes in gases (and not only in gases), it is convenient to use a graphical presentation of the equation of state in the form of curves showing how one of the parameters depends on another one at a given constant value of the third parameter. For example, at a given constant temperature, the dependence of the pressure of a gas on its volume has the form shown in Fig. 4, where the different curves correspond to different temperatures:

the higher the temperature, the higher is the curve on the graph. The state of the gas in such a diagram is depicted by a point. The curve of one parameter against another shows the change in the state, called a process in a gas. For instance, the curves in Fig. 4 show the process of expansion or compression of a gas at a given constant temperature.

In the following, we will use such graphs to a great extent in studying various processes in molecular systems.

An equation of state for ideal gases is easily obtained from the basic equations of the kinetic theory (1.4) and (1.5).

Indeed, introducing into Eq. (1.4) instead of the mean kinetic energy of molecules its expression from Eq. (1.5), we get

$$p = nkT \tag{1.6}$$

If the volume $V$ contains $N$ particles, then $n = N/V$; introducing this expression into Eq. (1.6), we get

$$pV = NkT \tag{1.7}$$

This equation, which includes all three parameters of state, is an equation of state of ideal gases.

It will be good to transform it, however, so that it will include the easily measurable mass $M$ of a gas instead of the number of particles $N$ that does not lend itself to direct measurement. We shall use the concept of a *gramme-molecule* or *mole* for this transformation. It should be remembered that a mole of a substance is such an amount of it whose mass expressed in grammes equals the relative molecular mass of the substance (sometimes the term "molecular weight" is used). This distinctive unit of the amount of a substance is remarkable for the fact that a mole of any substance contains the same number of molecules. Indeed, if we denote the relative masses of any two substances by $\mu_1$ and $\mu_2$, and the masses of molecules of these substances by $m_1$ and $m_2$, we can write the obvious equations

$$\mu_1 = m_1 N_1 \quad \text{and} \quad \mu_2 = m_2 N_2 \tag{1.8}$$

where $N_1$ and $N_2$ are the numbers of particles in a mole of these substances. Since from the definition of relative mass it follows that $\mu_1/\mu_2 = m_1/m_2$, then by dividing the first of equations (1.8) by the second, we get $N_1 = N_2$, i.e. a mole of any substance contains the same number of molecules.

The number of particles in a mole, identical for all substances, is called the *Avogadro constant*. We shall denote it by $N_A$. We can thus define the mole as a unit of a special quantity—the *amount of a substance*:

*1 mole is the amount of a substance containing a number of molecules* or other particles (for example atoms if a substance consists of atoms) *equal to the Avogadro constant.*

If we divide the number of molecules $N$ in a given mass of a gas by the Avogadro constant $N_A$, we get the number of moles in this mass of the gas.

But we can obtain the same quantity by dividing the mass $M$ of the gas by its relative mass $\mu$ so that

$$\frac{M}{\mu} = \frac{N}{N_A}, \qquad \text{whence} \qquad N = \frac{M}{\mu} N_A$$

Substituting this expression for $N$ in Eq. (1.7), we get the following form of the equation of state:

$$pV = \frac{M}{\mu} N_A kT \tag{1.9}$$

This equation includes two universal constants: the Avogadro constant $N_A$ and the Boltzmann constant $k$. Knowing one of them, for example the Boltzmann constant, we can determine the other (the Avogadro constant) by simple experiment using Eq. (1.9) for this purpose. To do this, we take a gas with a known value of its relative mass $\mu$, fill a vessel having a known volume $V$ with it, measure the pressure $p$ and temperature $T$ of the gas, and determine its mass $M$ by weighing the empty (evacuated) vessel and the vessel filled with the gas. The Avogadro constant $N_A$ was found equal to $6.02 \times 10^{23}$ mol$^{-1}$.

The most accurate value of the Avogadro constant at present is

$$N_A = 6.022\,091\,3 \times 10^{23} \text{ mol}^{-1}$$

The product of the universal constants $N_A k$ is also obviously a universal constant. It is called the *molar gas constant* or simply the *gas constant* and is usually denoted by $R$:

$$R = N_A k = 6.02 \times 10^{23} \times 1.38 \times 10^{-23} = 8.31 \text{ J/mol} \cdot \text{K} =$$

$$= 8.31 \times 10^7 \text{ erg/mol} \cdot \text{K}$$

(Its exact value is $R = 8.314\,41$ J/mol·K.)

Substituting the molar gas constant $R$ for $N_A k$ in Eq. (1.9), we get:

$$pV = \frac{M}{\mu} RT \tag{1.10}$$

The equation of state of an ideal gas written in this way is often called the *Clapeyron-Mendeleev equation*. The quantity $M/\mu$ in it is the number of moles in a given mass of a gas. For one mole of a gas, i.e. for the case when $M = \mu$, Eq. (1.10) becomes

$$pV = RT \tag{1.11}$$

## 1.5. IDEAL GAS LAWS

The laws controlling the behaviour of gases that have been known for a long time were discovered experimentally in their time (for instance

Boyle's law was established back in the 17th century). It is easy to see that all these laws can be obtained from the equations of the kinetic theory of gases given above.

**Boyle's Law.** Consider a gas in conditions when its temperature is kept constant (such conditions are called *isothermal*). If we assume in equation of state (1.11) that $T = \text{const}$, it is obvious that the entire right-hand side of the equation is a constant quantity so that

$$pV = \text{const} \tag{1.12}$$

This formula, called an *equation of an isotherm*, is an expression of Boyle's law, according to which at a constant temperature the compression and expansion of a gas, i.e. the change in its volume, is attended by such a change in the pressure that the product of the pressure and volume remains constant. A graph of $p$ against $V$ for different temperatures is shown in Fig. 4. A glance at Eq. (1.12) shows that these curves, called *isotherms*, are hyperbolas.

Boyle's law shows how the pressure of a gas changes with a change in its volume at a constant temperature and, of course, at a constant mass.

**Compressibility of an Ideal Gas. Isothermal Compressibility.** The property of a gas, like any other body, to change its pressure when its volume is changed is called *compressibility*. If the volume is so changed that the temperature of the gas remains constant, the compressibility is characterized by the *isothermal compressibility* $\varkappa$, which is defined as the *relative* change in volume causing a unit change in pressure. It is obvious that

$$\varkappa = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{1.13}$$

Here $\partial V$ is the change in the volume of the gas causing the pressure to change by $\partial p$, and $V$ is the initial volume (it is the ratio of the change in a quantity to its initial value that is called the relative change in the quantity). The subscript $T$ of the derivative shows that it is taken at $T = \text{const}$.

It is quite simple to calculate the value of $\varkappa$ for an ideal gas. From equation of state (1.10) we get, since $\frac{M}{\mu} RT = \text{const}$,

$$d(pV) = V\,dp + p\,dV = 0$$

whence

$$\varkappa = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{p} \tag{1.14}$$

The minus sign indicates that an *increase* in the volume results in *lowering* of the pressure.

The isothermal compressibility of an ideal gas thus equals the reciprocal of its pressure and is measured in $m^2/N$ in the SI system, and in $cm^2/dyn$ in the cgs system.

The value of $\varkappa$ naturally diminishes with increasing pressure because the greater the pressure, the smaller are the possibilities for the gas to become compressed still more.

**Gay-Lussac Law.** Let a gas now be in conditions when its pressure $p$ remains constant, but its temperature changes. Such conditions can be provided if we place a gas in a cylinder closed with a movable piston (Fig. 5). A change in the temperature in such a cylinder will cause the piston to move and the volume to change. The pressure will remain constant.

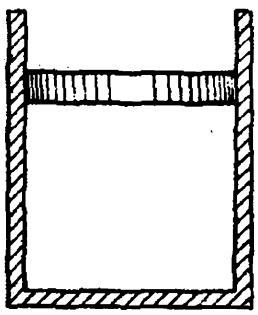


Fig. 5

It can be seen from equation of state (1.10) that in this case the ratio of the volume of the gas to its temperature will be constant:

$$\frac{V}{T} = \frac{M}{\mu}\frac{R}{p} = \text{const} \tag{1.15}$$

This equation, called an *equation of an isobar* (a process taking place at constant pressure is called *isobaric*), expresses the well-known law formulated by J. Gay-Lussac (it is sometimes called, though without sufficient grounds, Charles' law).

The graph of the isobar $V = f(T)$, as can be seen from Eq. (1.15), is a straight line emerging from the origin of coordinates.

**Cubic Expansion Coefficient of a Gas at Constant Pressure.** The cubic expansion coefficient $\alpha$ can be written in a form similar to the isothermal compressibility:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{1.16}$$

It follows from equation of state (1.10) that $\left(\frac{\partial V}{\partial T}\right)_p = \frac{M}{\mu}\frac{R}{p}$, whence

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T}$$

i.e. the cubic expansion coefficient of an ideal gas equals the reciprocal of the absolute temperature. At 0 °C, for example, it equals 1/273 $K^{-1}$.

**Isochoric Process.** When a gas is in conditions in which its volume remains constant (processes taking place in such conditions are called *isochoric*), then as can be seen from the equation of state of a gas (1.10), the change in the pressure of a gas when its temperature changes occurs so that the ratio $p/T$ remains constant:

$$\frac{p}{T} = \frac{M}{\mu}\frac{R}{V} = \text{const} \tag{1.17}$$

This statement, however, cannot be considered as a law of nature. The temperature scale of an ideal gas is constructed exactly on the basis of the assumption that $p/T = \text{const}$ (see Sec. 1.3). Hence, experimental verification of this "law" cannot give any other result.

**Avogadro Law.** The Avogadro law directly follows from the equation of state of an ideal gas. It states that *at identical pressures and temperatures, equal volumes of any gas contain an identical number of molecules.* Indeed, suppose we have two identical volumes of two different gases at identical pressures and temperatures. For each gas, we can write the equation of state in its form (1.7):

$$pV = N_1 kT \text{ and } pV = N_2 kT$$

where $N_1$ and $N_2$ are the number of molecules in each of the volumes. It directly follows from these two equations that

$$N_1 = N_2$$

This is the Avogadro law.

It evidently follows from this law that, conversely, different gases containing the same number of molecules will occupy identical volumes at the same pressures and temperatures. Therefore, a mole of any gas at a given pressure and temperature occupies an identical volume. In particular, at a temperature of 0 °C (273.15 K) and a pressure of 1 atm ($1.01 \times 10^5$ N/m$^2$), a mole of any gas occupies the volume

$$V_0 = \frac{RT}{p} \approx \frac{8.31 \times 273}{1.01 \times 10^5} \approx 2.24 \times 10^{-2} \text{ m}^3/\text{mol}$$

The exact value of $V_0 = 2.224\,138\,3 \times 10^{-2}$ m$^3$/mol.

It is also easy to calculate the number of molecules $n_0$ in 1 m$^3$ in these (so-called standard) conditions:

$$n_0 = \frac{N_0}{V_0} \approx \frac{6.02 \times 10^{23}}{2.24 \times 10^{-2}} \approx 2.7 \times 10^{25} \text{ m}^{-3}$$

This number is called the *Loschmidt number.*

**Dalton's Law.** Let a vessel having the volume $V$ contain a mixture of various gases that do not react chemically with one another and that are in a state of thermal equilibrium. For such a mixture, the equation of state has the form

$$pV = (N_1 + N_2 + N_3 + \ldots)kT$$

where $N_1, N_2, N_3, \ldots$ are the numbers of molecules of the corresponding components of the mixture. It is quite obvious that

$$N_1 + N_2 + N_3 + \ldots = N$$

where $N$ is the total number of molecules in the vessel.

The pressure of the gas is

$$p = \frac{N_1}{V} kT + \frac{N_2}{V} kT + \frac{N_3}{V} kT + \ldots$$

This expression shows that each group of molecules exerts a pressure not depending on the pressure exerted by the other molecules. This is due to the fact that in an ideal gas there is no interaction between its molecules; they are "unaware" of the existence of other molecules. The expressions

$$\frac{N_1}{V} kT = p_1, \quad \frac{N_2}{V} kT = p_2, \quad \frac{N_3}{V} kT = p_3, \ldots$$

are the pressure of each of the mixture components occupying the volume $V$, i.e. $p_1, p_2, p_3, \ldots$ are the *partial* pressures of the mixture components. It should be remembered that the partial pressure of a gas that is a component of a gas mixture is the pressure which would be exerted by the gas if it alone occupied the entire volume in which the mixture is.

Thus,

$$p = p_1 + p_2 + p_3 + \ldots$$

i.e. *the pressure of a mixture of gases equals the sum of the partial pressures of its components*. This is the essence of Dalton's law, which is true only for ideal gases.

Experiments show that at sufficiently high pressures (of the order of magnitude of scores of atmospheres) when gases may no longer be considered ideal, deviations are observed (in both directions) from Dalton's law.

Using the main results of the kinetic theory of gases, we have thus obtained the laws controlling the behaviour of gases that had been established long before the theory was developed. This to a certain extent confirms the truth of the theory and allows us to consider that it has been verified experimentally. This also indicates that the gas laws treated above relate only to ideal gases which, generally speaking, had not been known before the kinetic theory of gases appeared. Experiments do show that when conditions of ideality are not complied with, deviations from the gas laws are observed. We can therefore consider that strict observance of the above laws is a feature of the ideality of a gas. It is exactly for this reason that a gas obeying, for example, Boyle's or Gay-Lussac's laws is sometimes called ideal.

## 1.6. VELOCITIES OF GAS MOLECULES

The fundamental equation of the kinetic theory of gases establishes a relationship between the mean kinetic energy of translational motion of molecules and the absolute temperature:

$$\frac{m\overline{v^2}}{2} = \frac{3}{2} kT$$

Thus the mean square (effective) velocity of the molecules is also determined:

$$\sqrt{\overline{v^2}} = \bar{v} = \sqrt{\frac{\overline{3kT}}{m}} \tag{1.18}$$

which for a given gas (at a given value of the mass $m$ of a molecule) depends only on temperature. If we multiply the numerator and denominator of the fraction in the radicand of the right-hand side of Eq. (1.18) by the Avogadro constant, we get

$$\bar{v} = \sqrt{\frac{\overline{3RT}}{\mu}} \tag{1.19}$$

because $N_A k = R$ and $N_A m = \mu$. Since by equation of state (1.11) we have $pV = RT$, where $V$ is the volume occupied by a mole of a gas, Eq. (1.19) can be written as follows:

$$\bar{v} = \sqrt{\frac{\overline{3p}}{\rho}} \tag{1.20}$$

where $\rho$ is the density of the gas equal to $\mu/V$, i.e. to the mass of a mole divided by its volume.

Equation (1.20) shows that the mean square velocity of molecules can be calculated from data obtained in measuring purely macroscopic quantities — the pressure of a gas and its density. For example, the density of nitrogen at atmospheric pressure and a temperature of 0 °C equals 1.25 kg/m³. The mean square velocity of the nitrogen molecules in this case is

$$\bar{v} = \sqrt{\frac{\overline{3 \times 1.013 \times 10^5}}{1.25}} \approx 500 \text{ m/s}$$

The density of hydrogen in the same conditions is approximately one-fifteenth of that of nitrogen. Therefore, the mean square velocity of the hydrogen molecules will be almost four times greater and will equal about 2000 m/s.

It is interesting to note that the velocities of the molecules of a gas are close to the velocity of sound in the same gas. This is explained by the fact that sound waves are carried in a gas by its moving molecules. It is therefore not surprising that the velocity of sound $c$ in a gas is approximately determined by the equation

$$c = \sqrt{\frac{\overline{p}}{\rho}}$$

The experimental determination of the velocity of gas molecules is of great interest because this allows us to determine experimentally the value

of the Boltzmann constant $k$ whose significance in the kinetic theory is obvious. The first direct experimental determination of the velocity of gas molecules was conducted by O. Stern (1920).

**Stern's Experiment.** A top view of the arrangement used in the experiment is shown schematically in Fig. 6. Platinum wire $L$ coated with a layer of silver served as the source of particles (atoms in the given case) whose

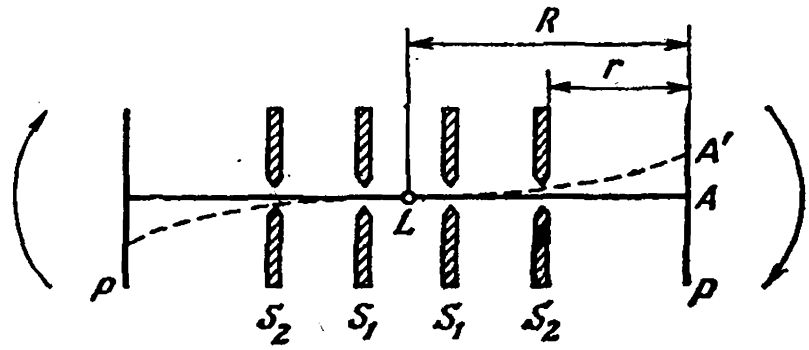



Fig. 6

velocity was studied. Wire $L$ was surrounded by two cylindrical diaphragms in which narrow slots $S_1$ and $S_2$ were cut so that the wire and the slots were in one vertical plane. This device was placed inside cylinder $P$ on whose inner surface opposite slot $S_2$ a removable brass plate serving as a target was placed. The entire system was placed under the bell of a pump creating a high vacuum (about $10^{-6}$ torr) and could rotate at a high velocity about the axis along which wire $L$ was stretched.

By passing an electric current through wire $L$, Stern heated it to a temperature at which silver appreciably evaporated (1235 K). Atoms of silver whose velocities corresponded to the temperature of the wire flew out in all directions. Part of the atoms passed through slots $S_1$ and $S_2$ that cut out from the stream of atoms a narrow sharply outlined beam consisting of particles travelling in the same direction and not colliding with one another (such directed streams of molecules bear the general name of *molecular beams*).

When the entire system was stationary, the atoms of silver forming the beam condensed on the target at the spot denoted by the letter $A$ in Fig. 6, forming on the target a stripe that was a resemblance of slot $S_2$. But when the device was brought into rotation, the atoms of the beam no longer struck the target at $A$, but were displaced from $A$ by a certain distance $\delta$ (in the figure $\delta = AA'$). The atoms, travelling with the velocity $v$, passed the entire distance $r$ from slot $S_2$ to the target during the time $t = r/v$. During this time, however, each point of the revolving cylinder was displaced over the distance $\delta$ determined by the expression

$$\delta = 2\pi nRt$$

where $n$ = number of revolutions of cylinder $P$ per second

$R$ = radius of this cylinder.
Substituting $r/v$ for $t$ in this expression, we get

$$\delta = \frac{2\pi nRr}{v} \tag{1.21}$$

When the device was rotated in the opposite direction, the stripe was displaced over the same distance to the other side of $A$. Thus two stripes were obtained on the target that were separated by the distance $2\delta$. This increased the accuracy of measuring $\delta$.

By measuring the distance between the stripes and knowing the values of $n$, $r$, and $R$, Stern used Eq. (1.21) to calculate the velocity $v$ of the atoms at the temperature of the wire.

The values of the velocities of atoms measured in this way were found to be close to the values calculated by Eq. (1.18).

The method of molecular beams developed by Stern is still being widely used for studying various properties of particles.

It is important to note that the displaced stripes obtained on the target in Stern's experiments were rather broad, blurred, and were not at all an image of the slot, in contrast to the sharp and narrow undisplaced stripe. This was to be expected, bearing in mind that the silver atoms fly out of the source with different velocities. It is clear that the quicker atoms reach the target with a smaller displacement relative to the place struck by the atoms when the device is not rotating than the slower atoms. The distance $2\delta$ between the stripes is the distance between those parts of them where the greatest density of the silver was observed and which, consequently, were struck by the greatest number of atoms.

It can be shown that atoms whose velocity is about 1.3 times greater than the mean square velocity will give the maximum density on the target. Therefore, the velocity $v$ calculated by Eq. (1.21) in which $\delta$ is half the distance between the densest parts of the silver deposits will be

$$v \approx 1.3\bar{v}$$

Having obtained the value of the mean square velocity from Stern's experiments described above, we can use Eq. (1.18) to determine the value of the Boltzmann constant. Stern's experiments make it possible not only to measure the mean square velocity, but also to roughly determine the distribution of atoms (or molecules) by velocities according to the blurring of the deposit on the target.

## 1.7. BROWNIAN MOVEMENT

One of the most convincing proofs of the reality of motion of molecules is the phenomenon of so-called *Brownian movement* discovered in 1827 by the British botanist Robert Brown when studying very tiny spores suspended

in water. When looking through a microscope having a high magnification, he found that the spores were in continuous chaotic motion, performing, as it were, a wild fantastic dance.

Further experiments showed that these movements are not connected with the biological origin of the particles or with any movements of the liquid. The movements are performed by any tiny particles suspended in a liquid or a gas. Such chaotic movements are performed, for example, by particles of smoke in still air. These chaotic movements of particles suspended in a liquid or a gas were called Brownian movement.

Special investigations showed that the nature of Brownian movement depends on the properties of the liquid or gas in which the particles are suspended, but does not depend on the properties of the substance which the particles themselves consist of. The velocity of the Brownian movement of particles grows with increasing temperature and with diminishing dimensions of the particles.

All these laws can easily be explained if we assume that the movements of the suspended particles appear owing to impacts received by them from moving molecules of the liquid or gas which they are in.

Naturally, every particle is subjected to such impacts from all sides. Upon the complete disorder of molecular movements, we could expect that the number of impacts received by a particle from one direction should exactly equal the number of impacts from the opposite direction so that all of them should completely compensate one another, and the particles should remain stationary.

This is exactly what occurs if the particles are not too small. But when we have to do with microscopic particles (from $10^{-4}$ to $10^{-5}$ cm in size), matters are different. It only follows from the fact that molecular movements are chaotic that *on an average* the number of impacts from different directions is the same. Deviations from the average values, however, are inevitable in such a statistical system as a liquid or a gas. Such deviations from the average or mean values of quantities which occur in a small volume or during a small interval of time are called *fluctuations*. If a body of an ordinary size is in a liquid or a gas, the number of impacts it receives from the molecules is so great that it is impossible to note either separate impacts or a random predominance of impacts in one direction over impacts in other directions. For tiny particles, however, the total number of impacts is comparatively small so that the prevalence of the number of impacts first in one direction and then in another one becomes noticeable. Moreover, it is exactly owing to such fluctuations of the number of impacts that the characteristic, as it were, convulsive movements of suspended particles appear which are called Brownian movement.

It is quite clear that Brownian movement is not the movement of molecules. What we see is not the result of the impact of one molecule, but rather the result of the number of impacts in one direction prevailing over

the number of impacts in the opposite direction. Brownian movement only very clearly reveals the existence of chaotic molecular movements.

Thus, Brownian movement is explained by the appearance of a resultant force having a definite direction owing to a chance difference between the number of impacts of molecules against a particle from different directions. Since the fluctuations usually last only a short time, then the direction of the resultant will change very rapidly, and together with it the direction of motion of the particle will change. This underlies the chaotic nature of Brownian movement which reflects the chaotic nature of molecular motion.

Let us now add a quantitative consideration of Brownian movement to the above qualitative explanation of it. Its quantitative theory was first given by A. Einstein and independently of him by M. Smoluchowski (1905). We shall derive the main relationship of this theory in a simpler way than the above-mentioned authors.

Owing to the incomplete compensation of the impacts of molecules against a Brownian particle, it is acted upon, as we have seen above, by a certain resultant force $F$ that causes it to move. In addition, the particle is also acted upon by the force of friction $f$ due to viscosity of the medium and directed oppositely to the force $F$.

We assume for simplicity that a particle has the shape of a sphere with the radius $a$. Hence, the force of friction $f$ can be expressed by the Stokes formula

$$f = 6\pi\eta a v$$

where $\eta$ = coefficient of internal friction of the liquid (or gas)
$v$ = velocity of the particle.

The equation of motion of the particle (Newton's second law) therefore has the form

$$m\ddot{\boldsymbol{r}} = \boldsymbol{F} - 6\pi\eta a\dot{\boldsymbol{r}} \tag{1.22}$$

Here $m$ = mass of a particle
$\boldsymbol{r}$ = radius-vector of the particle relative to an arbitrary system of coordinates
$\ddot{\boldsymbol{r}} = d^2\boldsymbol{r}/dt^2$
$\dot{\boldsymbol{r}} = d\boldsymbol{r}/dt = \boldsymbol{v}$ = velocity of the particle
$\boldsymbol{F}$ = resultant of the forces called forth by molecule impacts.

Let us consider the projection of the radius-vector $\boldsymbol{r}$ onto one of the coordinate axes, for example the $X$-axis. For this component, Eq. (1.22) becomes

$$m\ddot{x} = F_x - 6\pi\eta a\dot{x} \tag{1.23}$$

where $F_x$ is the component of the resultant force $\boldsymbol{F}$ along the $X$-axis.

Our task is to find the displacement $x$ of a Brownian particle imparted to it under the action of molecule impacts. Each particle constantly collides

with molecules after which it changes the direction of its motion. Different particles receive displacements that differ both in magnitude and in direction. The probable value of the sum of the displacements of all the particles is zero because there is equal probability of displacements having a positive or a negative sign. The mean value of the projection of the displacement of a particle $\bar{x}$ will therefore equal zero. The mean value of the *square* of the displacement will not equal zero, however, i.e. $\overline{x^2} \neq 0$, because $x^2$ does not change its sign when $x$ does. We shall therefore transform Eq. (1.23) so that it will include the quantity $\overline{x^2}$. For this purpose, we multiply both sides of the equation by $x$:

$$mx\ddot{x} = xF_x - 6\pi\eta a x\dot{x} \tag{1.24}$$

We use the obvious identities

$$x\ddot{x} = \frac{1}{2}\frac{d^2(x^2)}{dt^2} - \left(\frac{dx}{dt}\right)^2, \quad x\dot{x} = \frac{1}{2}\frac{d(x^2)}{dt}$$

Inserting these expressions into Eq. (1.24), we get

$$\frac{m}{2}\cdot\frac{d^2(x^2)}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = -3\pi\eta a\frac{d(x^2)}{dt} + xF_x$$

This equation holds for any particle, and, therefore, it also holds for the mean values of the quantities in it if averaging is performed for a sufficiently great number of particles. Hence, we can write

$$\frac{m}{2}\frac{d^2(\overline{x^2})}{dt^2} - m\overline{\left(\frac{dx}{dt}\right)^2} = -3\pi\eta a\frac{d(\overline{x^2})}{dt} + \overline{xF_x} \tag{1.25}$$

where $\overline{x^2}$ = mean value of the square of the displacement of a particle

$\overline{\left(\frac{dx}{dt}\right)^2}$ = mean value of the square of its velocity.

As regards the mean value of the quantity $\overline{xF_x}$ in the equation, it equals zero because for a large number of particles $x$ and $F_x$ take on positive and negative values with the same frequency.

Equation (1.25) therefore becomes

$$\frac{m}{2}\frac{d^2(\overline{x^2})}{dt^2} - m\overline{\left(\frac{dx}{dt}\right)^2} = -3\pi\eta a\frac{d(\overline{x^2})}{dt} \tag{1.26}$$

The quantity $\overline{\left(\frac{dx}{dt}\right)^2}$ in this equation is the mean value of the square of the projections of the velocity onto the $X$-axis. Since the movements of the

particles are random, the mean values of the squares of the projections of the velocity onto all three coordinate axes should be equal to one another, i.e.

$$\overline{\left(\frac{dx}{dt}\right)^2} = \overline{\left(\frac{dy}{dt}\right)^2} = \overline{\left(\frac{dz}{dt}\right)^2}$$

The sum of these quantities should also equal the mean value of the square of the velocity of the particles $\overline{v^2}$:

$$\overline{\left(\frac{dx}{dt}\right)^2} + \overline{\left(\frac{dy}{dt}\right)^2} + \overline{\left(\frac{dz}{dt}\right)^2} = \overline{v^2}$$

Consequently,

$$\overline{\left(\frac{dx}{dt}\right)^2} = \frac{1}{3}\overline{v^2}$$

Hence, the expression of interest to us in Eq. (1.26) is

$$m\overline{\left(\frac{dx}{dt}\right)^2} = \frac{1}{3}m\overline{v^2} = \frac{2}{3}\frac{m\overline{v^2}}{2}$$

The quantity $m\overline{v^2}/2$ is the mean kinetic energy of a Brownian particle. Upon colliding with molecules of a liquid or a gas, Brownian particles exchange their energy with them and are in thermal equilibrium with the medium in which they move. Therefore, the mean kinetic energy of translational motion of a Brownian particle should equal the mean kinetic energy of the molecules of the liquid (or gas), which, as we know, equals $3kT/2$:

$$\frac{m\overline{v^2}}{2} = \frac{3}{2}kT$$

and, consequently,

$$m\overline{\left(\frac{dx}{dt}\right)^2} = \frac{2}{3}\frac{m\overline{v^2}}{2} = kT \tag{1.27}$$

The circumstance that the mean kinetic energy of a Brownian particle equals $3kT/2$ (the same as for a gas molecule!) has a significance of principle. Indeed, the basic equation (1.5) which we derived on page 32 holds for any particles that do not interact with one another and perform chaotic movements. It is no difference whether these are invisible molecules or considerably greater Brownian particles containing thousands of millions of molecules. From the standpoint of the molecular-kinetic theory, a Brownian particle can be treated as a giant molecule. Hence, the expression for the mean kinetic energy of such a particle should be the same as for a

molecule. The velocities of Brownian particles, however, are naturally incomparably smaller than those of molecules in accordance with their greater mass.

Let us now return to Eq. (1.26) and, with a view to Eq. (1.27), rewrite it in the form

$$\frac{m}{2}\frac{d^2(\overline{x^2})}{dt^2} - kT = -3\pi\eta a\frac{d(\overline{x^2})}{dt}$$

This equation is simple to integrate. Assuming that $\frac{d(\overline{x^2})}{dt} = Z$, we get

$$\frac{m}{2}\frac{dZ}{dt} - kT = -3\pi\eta aZ$$

and after separating variables, our equation becomes

$$\frac{dZ}{Z - \frac{kT}{3\pi\eta a}} = -\frac{6\pi\eta a}{m}dt$$

Integrating the left-hand side of this equation within the limits from 0 to $Z$, and the right-hand side from 0 to $t$, we get

$$\int_0^Z \frac{dZ}{Z - \frac{kT}{3\pi\eta a}} = -\int_0^t \frac{6\pi\eta a}{m}dt$$

or

$$\ln\left(Z - \frac{kT}{3\pi\eta a}\right) - \ln\left(-\frac{kT}{3\pi\eta a}\right) = -\frac{6\pi\eta a}{m}t$$

Hence,

$$Z = \frac{kT}{3\pi\eta a}\left[1 - \exp\left(-\frac{6\pi\eta a}{m}t\right)\right] = \frac{d(\overline{x^2})}{dt}$$

It can easily be seen that in the usual conditions of an experiment the quantity $\exp\left(-\frac{6\pi\eta a}{m}t\right)$ is negligibly small. Indeed, the dimensions of Brownian particles do not exceed $10^{-4}$ cm, the viscosity of a liquid is customarily close to that of water, i.e. approximately equals $10^{-2}$ (in the cgs system of units), and the density of the substance of the particles is of the order of magnitude of unity. Bearing in mind that the mass of a particle $m$ is $\frac{4}{3}\pi a^3\rho$, we get such a value of the exponent $\frac{6\pi\eta a}{m}t$ when $t$ exceeds $10^{-5}$ s that the quantity $\exp\left(-\frac{6\pi\eta a}{m}t\right)$ may be disregarded. Hence, if the

time interval between consecutive observations of a Brownian particle exceeds $10^{-5}$ s, which is always the case, we have

$$\frac{d}{dt}(\overline{x^2}) = \frac{kT}{3\pi\eta a} \tag{1.28}$$

For finite intervals of time $\Delta t$ and the corresponding displacements $\Delta\overline{x^2}$, Eq. (1.28) can be rewritten in the form

$$\frac{\Delta\overline{x^2}}{\Delta t} = \frac{kT}{3\pi\eta a} \tag{1.29}$$

whence

$$\Delta\overline{x^2} = \frac{kT}{3\pi\eta a}\Delta t \tag{1.30}$$

*The mean value of the square of the displacement of a Brownian particle* during the time $\Delta t$ along the $X$-axis or any other axis is proportional to this time.

Equation (1.30) permits us to calculate the mean value of the square of the displacements, this value being taken for all the particles participating in the phenomenon. But this equation also holds for the mean value of the square of many consecutive displacements of a single particle during equal time intervals. From the experimental viewpoint, it is more convenient to observe the displacements of a single particle. Such observations were conducted by J. Perrin in 1909.

Perrin observed the motion of the particles through a microscope whose eyepiece was provided with a network of mutually perpendicular lines serving as a coordinate system. Using this network, Perrin noted on it the consecutive positions of a single selected particle through definite time intervals $\Delta t$ (for example 30 seconds). After connecting the points which showed the positions of the particle on the network, he obtained a picture similar to the one depicted in Fig. 7. The latter shows both the displacements of the particle and their projections onto the $X$-axis.

It must be noted that the movements of a particle are considerably more complicated than can be judged from Fig. 7 because the positions of the particle have been registered in it through rather large time intervals (about 30 seconds). If we diminish these intervals, each straight length in the figure will develop into just as intricate a zig-zag path as the entire figure shows.

As a result of his observations, Perrin was able to measure the displacements $\Delta x$ and calculate the mean value of their squares. The data of these measurements well agreed with Eq. (1.30), and this confirmed the correctness of the molecular-kinetic explanation of the Brownian movement phenomenon and, consequently, of the molecular-kinetic theory itself.

Equation (1.30) can be used to determine the Boltzmann constant $k$ if we know the values of the coefficient of internal friction (viscosity) $\eta$

of a liquid, its temperature $T$, and the radius of a particle $a$. The values of this constant obtained by Perrin and other investigators from such measurements are close to the value indicated above of $k = 1.380 \times 10^{-16}$ erg/K. It should be noted here that Perrin himself used the data he obtained to determine the Avogadro constant by the formula $N_A = R/k$ because the constant $R$ can be found from an equation of state.

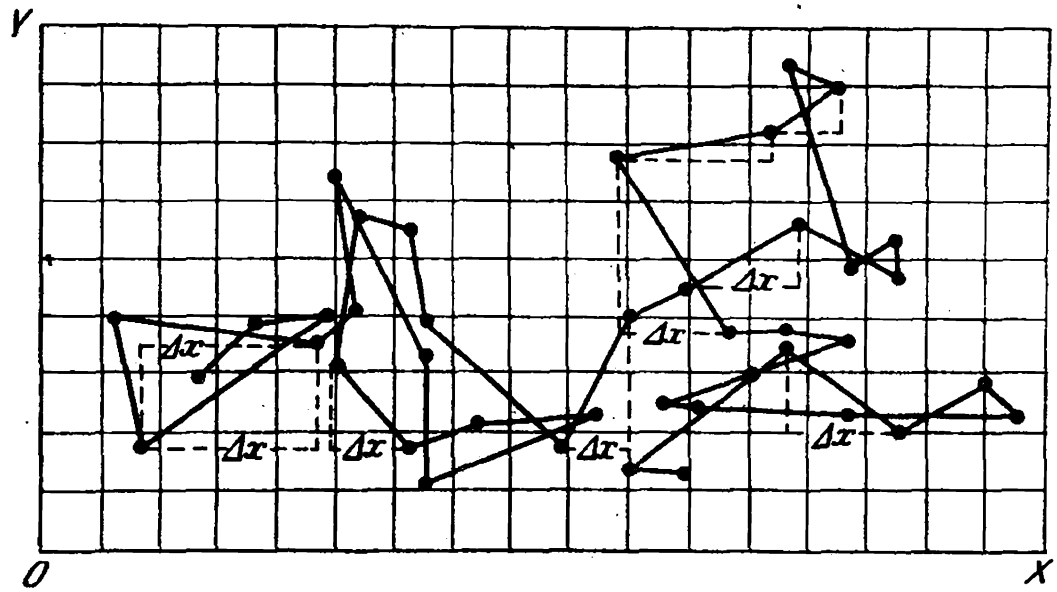



Fig. 7

Perrin's experiments had a great significance for the final substantiation of the molecular-kinetic theory.

## 1.8. BAROMETRIC FORMULA

Chaotic molecular movements result in the particles of a gas being uniformly distributed throughout the volume of a vessel so that each unit of volume contains on the average an identical number of particles. In an equilibrium state, the pressure and temperature of a gas are also the same throughout the entire volume. But this is how matters are only when no external forces act on the molecules. When such forces are present, molecular movements result in distinctive behaviour of gases.

Consider, for example, a gas (air) acted upon by the force of gravity. If there were no thermal motion of the molecules, all of them would "fall" onto the Earth under the action of the force of gravity, and all the air would be gathered in a very thin layer at the Earth's surface. If there were no force of gravity, but molecule movements did exist, the molecules would fly away to all parts of outer space. The atmosphere, the Earth's envelope of air, owes its existence in its present state to the simultaneous presence of both thermal motion of the molecules and forces of attraction to the Earth. A quite definite distribution of the molecules in altitude sets in in the atmosphere. In accordance with this distribution of the molecules,

there is a definite law of the change in the pressure of a gas with altitude which is simple to find.

Consider a vertical column of air (Fig. 8). Let the pressure at the Earth's surface, where $x = 0$, be $p_0$, and at the altitude $x$ be $p$. When the altitude changes by $dx$, the pressure changes by $dp$. The pressure of the air at a certain altitude equals the weight of a vertical column of air that is above a unit area at this altitude. Hence, $dp$ equals the difference between the weights of the column of air over a unit area at the altitudes $x$ and $x + dx$, i.e. equals the weight of a column of air having the altitude $dx$ and a base area equal to unity:

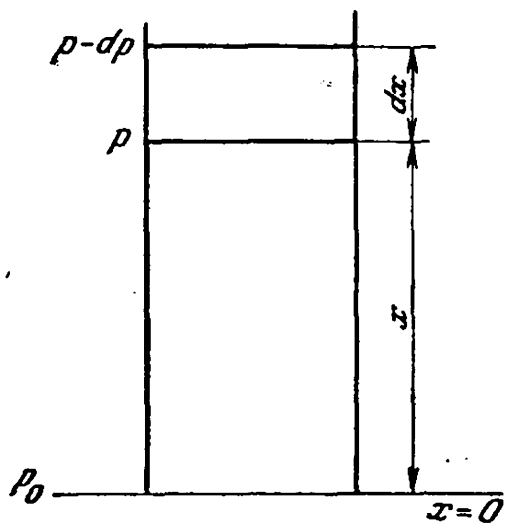



Fig. 8

$$dp = -\rho g\, dx$$

where $\rho$ = density of air (the mass of a unit volume)

$g$ = acceleration of gravity.

The density of a gas $\rho$ equals the product of the mass $m$ of a molecule and the number of molecules $n$ in a unit volume:

$$\rho = mn$$

It is known from the kinetic theory [Eq. (1.6)] that $n = p/kT$. Consequently, $\rho = mp/kT$ and

$$dp = -\frac{mg}{kT} p\, dx$$

This equation, to separate the variables, can be rewritten in the form

$$\frac{dp}{p} = -\frac{mg}{kT} dx \tag{1.31}$$

If we assume that the temperature at all altitudes is the same (which, generally speaking, is not true), then by integrating Eq. (1.31) we get

$$\ln p = -\frac{mg}{kT} x + \ln C \tag{1.32}$$

where $C$ is an integration constant. Hence,

$$p = C \exp\left(-\frac{mg}{kT} x\right) \tag{1.33}$$

The constant $C$ is determined from the condition that when $x = 0$ the pressure $p = p_0$. Using these values of $x$ and $p$ in Eq. (1.33), we get

$$C = p_0$$

Therefore, the dependence of the pressure of the air on the altitude of interest to us has the form

$$p = p_0 \exp\left(-\frac{mg}{kT}x\right) \tag{1.34}$$

or, taking into consideration that $m = \mu/N_A$ (where $\mu$ is the mass of a mole, or the molecular mass, and $N_A$ is the Avogadro constant), we get

$$p = p_0 \exp\left(-\frac{\mu g}{RT}x\right) \tag{1.35}$$

Equation (1.34) establishing the law of the drop in pressure with altitude is called the *barometric formula.* It shows that the pressure of a gas diminishes with altitude according to an exponential law. The latter is used to determine the altitude by measuring the pressure at the given altitude and at sea level (it is naturally sufficient to measure the latter pressure once).

The instruments used for measuring the altitude of mountain peaks, aircraft, etc. are special barometers graduated directly in metres. For this purpose, however, a correction must be introduced into Eq. (1.34) for the temperature, which decreases with increasing altitude, whereas we have obtained the barometric formula assuming that the temperature is constant at all altitudes.

The barometric formula (1.34) can also be used to determine the Boltzmann constant $k$, but the accuracy in this case is not high exactly because of the temperature correction.

Since the pressure of a gas, as we have seen earlier, is proportional to the number of molecules $n$ in a unit volume ($p = nkT$), then formula (1.34) also expresses the law of diminishing of the density of molecules with altitude:

$$n = n_0 \exp\left(-\frac{mg}{kT}x\right) \tag{1.36}$$

where $n$ and $n_0$ are the numbers of molecules in a unit volume at points the difference between whose altitudes is $x$. This formula, like Eq. (1.35), shows that the Earth's atmosphere should extend to infinity.

In deriving the barometric formula (1.34) or (1.36), we assumed that the acceleration of gravity $g$ is constant, i.e. does not depend on the altitude $x$. This is the reason why in integrating Eq. (1.31) we carried $g$ out of the integral sign. Such a simplification can be accepted for comparatively small values of $x$ (of the order of magnitude of scores of kilometres). For high altitudes, account must be taken of the fact that the acceleration of gravity diminishes with an increasing distance from the Earth's surface.

Indeed, from the law of universal gravitation, it follows that at a distance $r$ from the Earth's centre the acceleration of gravity is

$$g(r) = \gamma \frac{M}{r^2} = \gamma \frac{M}{(r_0 + x)^2}$$

where $\gamma$ = gravitational constant (in the SI system $\gamma = 6.67 \times \times 10^{-11}\,\mathrm{N \cdot m^2/kg^2}$, and in the cgs system $\gamma = 6.67 \times \times 10^{-8}\,\mathrm{dyn \cdot cm^2/g^2}$)

$M$ = Earth's mass

$r_0$ = Earth's radius.

Therefore, Eq. (1.31) must be rewritten in the form

$$\frac{dp}{p} = -\gamma \frac{Mm}{kT} \frac{dx}{(r_0 + x)^2}$$

After integration, we get

$$\ln p = \gamma \frac{Mm}{kT} \frac{1}{r_0 + x} + \ln C$$

or

$$p = C \exp\left(\gamma \frac{Mm}{kT} \frac{1}{r_0 + x}\right) = C \exp\left(\gamma \frac{M}{r_0^2} \frac{m}{kT} \frac{r_0^2}{r_0 + x}\right) =$$

$$= C \exp\left(\frac{mg}{kT} \frac{r_0^2}{r_0 + x}\right) \tag{1.37}$$

The integration constant $C$ is determined from the condition that when $x = 0$ the pressure $p = p_0$. Introducing these values of $x$ and $p$ into Eq. (1.37), we get:

$$C = p_0 \exp\left(-\frac{mgr_0}{kT}\right)$$

and the dependence of the pressure on the altitude acquires the final form

$$p = p_0 \exp\left[-\frac{mgr_0}{kT}\left(1 - \frac{r_0}{r_0 + x}\right)\right] \tag{1.38}$$

At first appearances, a paradoxical result follows from this equation, namely, that even at an infinitely remote distance from the Earth, i.e. when $x \to \infty$, the pressure does not equal zero:

$$p_\infty = p_0 \exp\left(-\frac{mgr_0}{kT}\right)$$

This means that the Earth's atmosphere (like that of other planets) should extend to infinity, and the density of the gas should not equal zero anywhere. Since this is physically impossible (the number of molecules is

finite while the volume of the Universe is infinite), we have to assume that the Earth's atmosphere is not in the equilibrium state. The lack of equilibrium consists in that the atmosphere's gas is continuously dispersing into outer space. This, however, did not result (and during many hundreds of millions of years will not result) in the Earth losing its atmosphere because only a negligible fraction of the particles of the air escape from the Earth's atmospheric envelope. But such a state could have resulted, for instance, in the Moon losing its atmosphere if it ever had had one in the past (this will be described in greater detail on a later page).

**Perrin's Experiment.** Equation (1.36) was used by Perrin for experimental verification of the barometric formula and for determining the Boltzmann constant (or, which is the same, the Avogadro constant).

Perrin took advantage of the fact that, as shown by his experiments with Brownian movement, small suspended particles can be treated like uninteracting molecules of very great dimensions. It can therefore be expected that particles of the Brownian type suspended in a liquid and subjected to the action of the force of gravity will be distributed in height in the same way as the molecules of a gas, i.e. according to the law given by Eq. (1.36).

Perrin prepared emulsions (an emulsion consists of two immiscible liquids of which one forms fine droplets suspended in the other) containing particles of about the same size and having an approximately spherical shape. A microscope with a very small depth of field set up vertically (Fig. 9) was used to observe the distribution of the suspended particles in height. For this purpose, the microscope was focussed on layers of the emulsion at different heights (depths). Particles in a layer not over 0.001 mm deep were in the field of vision of the microscope while the particles above and below them were not visible at all. The number of particles in the field of vision was not great so that it was possible to count them. This number is proportional to the number of particles $n$ in a unit volume. The measurements were conducted many times, and the mean value of many measurements was determined. The total number of particles counted in some series of experiments reached many thousands. These measurements showed that the concentration of the particles does diminish with the height according to the exponential law expressed by Eq. (1.36) in which, however, the loss of weight of a particle in accordance with Archimedes' principle is taken into account.

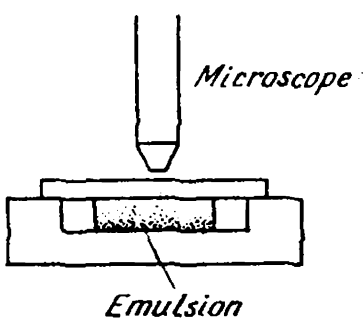


Fig. 9

If the mass of a particle is $m$, then its weight with account of Archimedes' buoyancy is

$$mg\left(1-\frac{\rho}{\rho_0}\right)$$

where $\rho_0$ = density of the substance of a particle

$\rho$ = density of the liquid in which it is suspended.

Equation (1.36) therefore becomes

$$n = n_0 \exp\left[-\frac{mg\left(1-\frac{\rho}{\rho_0}\right)}{kT}x\right] \tag{1.39}$$

It follows from Eq. (1.39) that if we count the number of particles $n_1$ and $n_2$ in the field of vision of the microscope in two layers of the emulsion $x_1$ and $x_2$, then from the relationship

$$\frac{n_1}{n_2} = \exp\left[-\frac{mg\left(1-\frac{\rho}{\rho_0}\right)}{kT}(x_1 - x_2)\right] \tag{1.40}$$

it is not difficult to determine the Boltzmann constant $k$ if we measure the mass of the particles $m$, their density $\rho_0$, the density of the liquid $\rho$, and the temperature $T$. The last two quantities are measured by generally known procedures. It was difficult to measure the mass and density of the emulsion particles owing to their small (microscopic!) dimensions.

Perrin determined the density of the substance of the particles by measuring the mass and volume of the emulsion. For this purpose, the mass $M_0$ of the water filling a definite vessel (a pycnometer) was first determined by weighing. Next, the volume of the pycnometer $M_0/\rho_1$ (here $\rho_1$ is the density of water) was calculated. After this, the mass $M$ of the emulsion (in water) filling the same pycnometer was found. Then, the pycnometer with the emulsion was placed in a kiln where the liquid was completely evaporated; the pycnometer was again weighed, and as a result the mass $M_2$ of the particles in the emulsion was found. From these measurements, the volume of the water in the emulsion was found:

$$V_{\text{wat}} = \frac{M_1 - M_2}{\rho_1}$$

the volume of the emulsion particles:

$$V_{\text{em}} = \frac{M_0}{\rho_1} - \frac{M_1 - M_2}{\rho_1}$$

and, consequently, the density $\rho_0$ of the substance of the particles:

$$\rho_0 = \frac{M_2}{V_{\text{em}}} = \frac{M_2\rho_1}{M_0 - M_1 + M_2}$$

Perrin determined the radius of the emulsion particles, which were almost regular spheres, by measuring the velocity $v$ of their fall in the emulsion filling a capillary tube. A sphere with the radius $a$ falling with the velocity

$v$ in a liquid whose viscosity is $\eta$ is acted upon by the force of friction directed vertically upward and equal to

$$F = 6\pi\eta a v$$

In addition, the falling sphere is acted upon by an Archimedian force directed upward and equal to

$$\frac{4}{3}\pi a^3 \rho g$$

where $\rho$ is the density of the liquid, and, of course, by the force of gravity

$$mg = \frac{4}{3}\pi a^3 \rho_0 g$$

where $\rho_0$ is the density of the substance of the sphere. The resultant of the last two forces

$$F_1 = \frac{4}{3}\pi a^3 (\rho_0 - \rho) g$$

causes the sphere to travel with an acceleration $g$ directed downward ($\rho_0 > \rho$). But as the velocity of the sphere grows, the force of friction $F$ retarding it also grows. As a result, the sphere acquires such a constant velocity at which

$$6\pi\eta a v = \frac{4}{3}\pi a^3 (\rho_0 - \rho) g \tag{1.41}$$

This is the velocity that was measured by Perrin. Equation (1.41) is used to find the radius of a particle and, correspondingly, its mass:

$$a = \sqrt{\frac{9\eta v}{2g(\rho_0 - \rho)}}, \quad m = \frac{4}{3}\pi a^3 \rho_0$$

Thus all the quantities in Eq. (1.40) lend themselves to measurement.

After taking logarithms of Eq. (1.40), the equation for calculating the Boltzmann constant has the form

$$k = \frac{m\left(1 - \frac{\rho}{\rho_0}\right) g(x_2 - x_1)}{T \ln\left(\frac{n_1}{n_2}\right)}$$

The value of $k$ obtained from Perrin's experiments is somewhat smaller than the value adopted at present. After Perrin, other investigators used his method to obtain a more accurate value.

## 1.9. BOLTZMANN LAW

The barometric formula obtained above relates to the case when a gas is under the action of the force of gravity. The quantity $mgx$ in Eq. (1.36):

$$n = n_0 \exp\left(-\frac{mg}{kT}\, x\right)$$

is the potential energy of a molecule at the altitude $x$. We can therefore say that Eq. (1.36) gives us the number of particles whose energy $U = mgx$ if the number of particles whose energy is zero equals $n_0$ (the altitude $x$ is counted from zero). There are no grounds to consider that the behaviour of a gas will change appreciably if instead of the force of gravity some other force acts on it, and the expression for the energy has a different form. If a gas is in a force field so that its particles have a certain potential energy, the number of particles having the given energy $U$ is

$$n = n_0 \exp\left(-\frac{U}{kT}\right) \tag{1.42}$$

Equation (1.42) is called the *Boltzmann equation*. It allows us to determine the fraction of particles which in conditions of thermal equilibrium have the energy $U$:

$$\frac{n}{n_0} = \exp\left(-\frac{U}{kT}\right) \tag{1.43}$$

A glance at Eq. (1.43) shows that the fraction $n/n_0$ of particles having the given energy $U$, apart from the magnitude of this energy, depends only on the temperature. This allows us to treat the temperature itself in a somewhat different way, namely, like a quantity on which the distribution of the particles by energies depends.

At a given temperature, the fraction of molecules having the energy $U$ depends on its value and rapidly diminishes with a growth in $U$. This means that the fraction of molecules having a very high energy is always very small. And the lower the temperature, the higher is the rate at which $n/n_0$ diminishes with a growth in $U$.

## 1.10. CONCEPT OF PROBABILITY

It is convenient to treat the Boltzmann law, like the barometric formula, from a somewhat different viewpoint using the concept of *probability*.

We resort to this term, in contrast to "authenticity" or "determinacy", when we are dealing with random events, i.e. such events the conditions for whose occurrence are unknown for some reason or other, and which therefore cannot be predicted with certainty beforehand.

When acquiring, for example, a ticket in a trolleybus, we do not know beforehand whether its number will be even or odd. Therefore such an event as the acquiring of a ticket having an even number may be considered as a random event. If we acquired, for instance, 10 tickets (not at the same time, of course), among them may be three, and six, and eight tickets with even numbers. But it may also happen that there will not be a single ticket with an even number among them, or, conversely, all 10 tickets will have even numbers.

There is a definite law, however, in this seemingly complete arbitrariness. It consists in that if we repeat our experiment (acquiring tickets) a sufficiently great number of times, then in about one-half of the total number of cases our ticket will have an even number. And the greater the number of such "experiments" or "trials", the closer to one-half will the fraction of tickets with even numbers be. In this case, the *probability* of acquiring a ticket with an even number is said to equal one-half.

In the same way, if we toss a coin many times, we can be sure that it will fall heads up in about half of all the cases. And the probability of this happening will be the greater, the greater is the number of times we toss the coin.

This and other similar experiments permit us to define probability as follows: *the probability of an event is the limit which the ratio of the number of trials resulting in occurring of the event to the total number of trials upon an infinite growth of the latter tends to.*

If of $N$ trials (or observations) $N'$ result in occurrence of the event we are interested in, the probability $P$ of this event is expressed by the equation

$$P = \lim_{N \to \infty} \frac{N'}{N}$$

In the example with the ticket numbers described above, the probability of an even number is 1/2. This, naturally, is also the probability of an odd number. The sum of these two probabilities equals unity. It gives us the probability of the event that a ticket will have either an even or an odd number. But such an event is inevitable so that a probability equal to unity denotes authenticity. Conversely, if an event is impossible (for example no number on a ticket), its probability equals zero.

In the example with the tickets (like the tossing of a coin), a "trial" (acquiring a ticket) may have one of two results: the number of the ticket may be even or odd, and both these results are equally possible. But this is not always the case. For example, from the fact that two results are possible when shooting at a target — a hit or a miss, it does not follow that the probability of a hit is 1/2 because a hit and a miss are not equally possible results of a shot. And if a very great number of shots are made, the ratio of the number of hits to the number of shots will hardly equal one-half. For a highly skilled marksman having a well-sighted rifle, it will be close to unity while for a poor shot it may differ only slightly from zero. Although

the probability of each of the two results of a shot, however, does not equal 1/2, their sum (for a given person) in this case will also equal zero — we can say with certainty that every shot will be either a hit or a miss!

**Theorem of Summation of Probabilities.** Let us now consider another example that will permit us to formulate one of the important laws of the theory of probability and, in addition, give another definition of the magnitude of the probability itself. It will be useful to us in the following.

Assume that a box contains 20 smooth balls of the same size and weight, of which 5 are white and the others are black. If we now extract one ball from the box, it is quite obvious that since the balls do not differ from one another in anything except colour, the probability of extracting one of the balls equals that of extracting another one. For each ball which we would like to note in some way, the probability of being extracted is 1/20.

Let us now see what the probability is of extracting a white ball. Since the probability of extracting any ball (white or black) is 1/20, and the number of white balls is five (and it is no difference to us which of them will be extracted), the required probability will equal the sum of the probabilities for all the white balls:

$$P = \frac{1}{20} + \frac{1}{20} + \frac{1}{20} + \frac{1}{20} + \frac{1}{20} = \frac{5}{20}$$

This result expresses one of the important postulates of the theory of probability — the theorem of summation of probabilities, which states that *if $P_1$, $P_2$, $P_3$, etc. are the probabilities of several mutually exclusive events, then the probability that one of them will happen is the sum of the probabilities of happening for these separate events.*

Hence, the sum of the probabilities of several events gives us the probability that either one, or a second, or a third, etc. of these events will happen. It is assumed that these events, or at least two of them, cannot occur simultaneously. Thus, in our example, 5/20 is the probability that a white ball will be extracted, and since the operation of extracting a ball is performed only once, then if one white ball is extracted, no other ball can be extracted from the box.

The above example permits us to give a new definition of probability that differs somewhat from the previous one. We found that the probability of extracting a white ball is 5/20. But 20 is the number of all possible results of the ball extracting operation while 5 is the number of cases (from the 20 possible) favouring the given event — the extraction of a white ball. This allows us to define the probability of a given event as the *ratio of the number of cases favouring it to the total number of cases that may happen provided that all the cases are equally possible.*

This definition of probability belongs to P. Laplace. It is easy to see that it does not contradict the previous definition. For the last definition of probability, it is important that all the cases be equally possible, i.e. equally probable. This is exactly how matters were in our example with the balls.

We usually also have to deal with equally probable events when we apply the theory of probability to physics.

Let us now return to the equation of Boltzmann's law (1.43). It follows from what we have said here about probability that the quantity $n/n_0$ in this equation has the meaning of probability. We can see that any of the $n_0$ molecules can have the potential energy $U$. Hence, $n_0$ is the total number of possible events. Actually $n$ molecules have the energy $U$. Therefore, $n$ is the number which we earlier called the number of "favouring" cases. This is why the ratio $n/n_0$ which we called (and with every right) the fraction of the molecules having the energy $U$ is also the probability of the fact that any of the $n_0$ molecules has such an energy.

**Theorem of Multiplication of Probabilities.** One more important postulate of the theory of probability — the theorem of multiplication of probabilities — remains to be considered. It relates to the case when the probability of a *complex* event consisting in the simultaneous happening of two or more independent events is being determined. Events are called *independent* if the probability of any one of them does not depend on whether any other one of them will happen.

Returning to our previous examples with tickets and a marksman, we can, for instance, pose the following problem: what is the probability that a marksman going to the shooting-range by trolleybus will acquire a ticket with an even number and after this his first shot will be a hit? It is clear that these two events are independent.

Assume that for our marksman the probability $P_1$ of hitting the target is 0.8. This means that in an average of 10 visits to the shooting-range his first shot will hit the target in eight cases. But only in one-half of them will he acquire a ticket with an even number on his way because the probability $P_2$ of getting a ticket with such a number is 1/2. Hence, the required probability $P_{12}$ of the complex event (or set of events) — the coinciding of an even number and a successful shot — equals the product of the probabilities of each of them:

$$P_{12} = P_1 P_2 = 0.8 \times 0.5 = 0.4$$

*The probability of the simultaneous happening of two or several independent events equals the product of the probabilities of each of them happening separately.*

**Probability and Mean Values of Quantities.** In the preceding sections, we have repeatedly used the mean values of various physical quantities characterizing the motion of molecules: the mean velocity, mean energy, etc. We resorted to this procedure for describing molecular systems because in view of the great number of particles which they consist of, there is neither the possibility nor the need to consider quantities relating to each one separately. We have seen that the use of mean values of quantities did not hinder our obtaining quite accurate laws such as the equation of state of an ideal gas.

It is not difficult to see that the mean values of physical quantities are also closely related to the concept of probability.

Owing to the continuous chaotic movements of particles, any molecular system during a sufficiently long time interval should pass through an infinite number of states superseding one another in a very intricate way because of the numerous molecular interactions. During this long time, our system will be in each of the states not once, but many times.

Suppose we have to determine a quantity $a$ relating to a system or to any part of it. For this purpose, we must perform (mentally, of course) many observations of the system in various states of it. Let the number of these observations be $N$. In $N_1$ observations (of a total of $N$), we shall find that the quantity interesting us has the value $a_1$; $N_2$ observations give us $a_2$ as the value of $a$, etc. The mean value of $a$, by definition, is

$$\bar{a} = \frac{N_1 a_1 + N_2 a_2 + N_3 a_3 + \ldots}{N_1 + N_2 + N_3 + \ldots} = \frac{\Sigma N_i a_i}{\Sigma N_i}$$

Since the sum $\Sigma N_i = N_1 + N_2 + \ldots$ equals the total number of observations $N$, then

$$\bar{a} = \frac{N_1}{N} a_1 + \frac{N_2}{N} a_2 + \ldots = \sum \frac{N_i}{N} a_i$$

But $N_1/N$, i.e. the ratio of the number of observations at which the quantity $a$ has the value $a_1$ to the total number of observations $N$, is the probability of our obtaining this value. In exactly the same way, $N_2/N$ is the probability of the fact that the value of $a$ obtained will be $a_2$, etc. Therefore, *the mean value of the quantity a equals the sum of the products of its separate values and their respective probabilities:*

$$\bar{a} = P_1 a_1 + P_2 a_2 + P_3 a_3 + \ldots = \Sigma P_i a_i$$

We have already noted that the laws of molecular physics always involve probability, but this never causes them to lose their accuracy or definiteness. The reason is that for any system in unchanging external conditions the physical quantities describing it are also virtually constant and equal to their mean values. In such cases, the system is said to be in a state of equilibrium. This will be considered in greater detail below.

### 1.11. CONCEPT OF DISTRIBUTION. DISTRIBUTION FUNCTION

The fundamental equations of the kinetic theory of ideal gases include, among other quantities, the mean kinetic energy of the molecules. This energy, in turn, is determined by their mean square or effective velocity. The meaning of the mean square velocity consists in that it is the velocity which all the molecules ought to have (if their velocities were identical in value and had equally probable directions) for the pressure of a gas to

be what it actually is. We know, however, that the velocities of molecules are not identical, and we even took this into consideration when deriving the fundamental equation. This is also indicated by experimental facts.

For example, in Stern's experiments, in which the velocity of molecules was measured, the displaced stripe was not sharp, but blurred owing to the fact that molecules having different velocities struck different spots of the target. This is also witnessed by the law of distribution of molecules in altitude in a gravitational field (the barometric formula) considered in Sec. 1.8. If all molecules had identical velocities, the distribution would be absolutely different. Indeed, let us assume that all the molecules at the Earth's surface have identical velocities whose vertical component equals $u$. These molecules would rise to the altitude $x$ determined by the condition

$$\frac{mu^2}{2} = mgx$$

i.e. to the altitude

$$x = \frac{u^2}{2g}$$

after which they would return to the Earth with their initial kinetic energy, i.e. they would behave like any body thrown vertically upward does. In such conditions, the atmosphere would abruptly terminate at the altitude $x$, and there would be no atmosphere above this altitude. Experience shows, however, that the atmosphere has no sharp boundary, its density diminishes with increasing altitude in accordance with the barometric formula. The assumption that all molecules have equal velocities thus contradicts experimental data.

Owing to the chaotic movements of the molecules and their collisions with one another, the molecules of a gas are distributed in some way or other by velocities so that they include both very rapid and very slow ones. Notwithstanding the complete state of chaos in molecular movements, notwithstanding the random nature of collisions and the changes in the velocities of molecules they cause, both theory and practice show that the distribution of molecules by velocities is not random, is not arbitrary, but is rather quite definite. Its nature is not affected by collisions between molecules or even by external fields. It is found to be unambiguous and the only one possible. And this not only fails to contradict our notion of the chaotic nature of molecular movements, but is due to it.

Before beginning to derive the law of distribution of molecules by velocities, let us determine the essence of the problem of distribution. The determination of the distribution of molecules by velocities seems to mean the determination of the number of molecules having a given velocity. A problem posed in this way, however, is deprived of meaning because the probable number of molecules having exactly (mathematically exactly!)

a given velocity equals zero. The number of different values of the velocity is infinitely great. The number of molecules, however, is finite. Hence, the number of molecules falling to the share of each arbitrarily given value of the velocity equals zero. Consequently, the problem should be posed in a different way: how many molecules (or what fraction of the molecules) have velocities within a certain interval near the preset velocity?

Statistical problems are always posed in exactly this way. If, for example, it is necessary to find the distribution of a country's population by ages, this does not mean that we have to determine the probable number of people having a certain exact (mathematically exact) given age. This has no sense because the number of different values of age is infinitely great whereas the number of people is finite. We can only determine the probable number of people whose age is within a definite interval of values. When in everyday life we say that so-and-so is 18 years old, we do not want to say that he is exactly 18 years, 0 days, 0 hours, 0 minutes, and 0 seconds old. Our statement only means that his age is within 18 and 19 years. In exactly the same way when, for instance, the Ministry of Education in planning the work of schools during a school year is interested in the number of seven-year-old children who will start going to school, it does not want to know the number of children who will become exactly seven years old at 8 a.m. on September 1. What it wants to know is the number of children whose age is between seven and eight years.

**Distribution Function.** When studying the distribution of particles by velocities, we will also seek the number of them whose velocities (or velocity components) are within a definite interval of velocity (or velocity component) values.

The number of particles $\Delta n$ in a unit volume whose velocities are within the interval from $v$ to $v + \Delta v$ is the greater, the bigger is the interval, i.e. $\Delta n$ is proportional to $\Delta v$, or

$$\Delta n = a \Delta v \tag{1.44}$$

where $a$ is a proportionality factor.

The quantity $\Delta n$ also depends on the velocity itself because the number of particles will differ in identical intervals between different absolute values of the velocity, just like the number of people in the age interval from 99 to 100 years old differs from the number of people whose age is between 30 and 31 years, although the size of the intervals in both cases is the same. This means that in Eq. (1.44) the proportionality factor should be a function of the velocity:

$$a = f(v)$$

Finally, the quantity $\Delta n$ should also be proportional to the number of particles $n$ in a unit volume. Therefore, the formula for $\Delta n$ should have the form

$$\Delta n = nf(v) \Delta v$$

It is usually written as follows:

$$\frac{\Delta n}{n} = f(v)\,\Delta v \tag{1.45}$$

The quantity $\Delta n/n$ in this equation is the fraction of particles in a unit volume of a gas whose velocities are within the interval from $v$ to $v + \Delta v$.

The function $f(v)$ is called the *distribution function*. Our task is to find the form of this function. Its meaning is clear from Eq. (1.45). Indeed, when $\Delta v = 1$, we have

$$f(v) = \frac{\Delta n}{n}$$

This means that $f(v)$ equals the fraction of particles whose velocities are within a *unit* interval of velocities near the velocity $v$.

Passing over to the limit, we can rewrite Eq. (1.45) in the form

$$\frac{dn}{n} = f(v)\,dv \tag{1.46}$$

It follows from what has been said above about probability that the quantity $dn/n$ in Eq. (1.46) has the meaning of probability: it is the probability of the fact that any of the molecules of a gas contained in a unit of its volume has a velocity that is within the interval $dv$ near the velocity $v$. We can assign to the value of the distribution function $f(v)$ the meaning of the probability of any molecule of a gas in a unit of its volume having a velocity that is within a *unit* interval near the velocity $v$. It is therefore called the *probability density*.

The barometric formula obtained in a previous section owes its appearance to the fact that the velocities of molecules are not the same, but are distributed in a definite way by their values. The nature of this distribution depends on the form of the function $f(v)$. Using the known barometric formula, we determine the form of the distribution function that gives us Eq. (1.36) showing how the density of molecules depends on the altitude:

$$n = n_0 \exp\left(-\frac{mg}{kT}\,x\right)$$

It should be noted that the distribution function can also be found in other ways. J. Maxwell obtained it (1859) using considerations based on the theory of probability. L. Boltzmann (1877) derived this function when studying the collisions of gas molecules owing to which the distribution sets in. The barometric formula can also be obtained as a result of this formula. For purposes of simplicity, however, we shall use the already derived barometric formula to find the distribution law.

## 1.12. DISTRIBUTION OF MOLECULES BY VELOCITY COMPONENTS

Imagine a vessel with a gas placed in empty space in a gravitational field. The gas in the vessel is in equilibrium, and its molecules are distributed by velocities in some way or other. Our task is to find this distribution. If at a certain moment of time the vessel is broken, then the gas molecules will begin to move in all directions, in particular also upward, against the direction of the force of gravity. The presence of the force of gravity will be what will help us to find the distribution that had existed in the gas before the vessel was broken.

Let us direct one of the coordinate axes, for example the $Z$-axis, vertically with its origin at the place where the vessel is. It is quite clear that the force of gravity will affect only the $z$-component of the velocity of the molecules so that we shall find the distribution of the molecules not by velocities, but by the values of the velocity component $v_z$.

Upward motion of the molecules along the $Z$-axis is attended by a decrease in the $z$-component of their velocity. If, for instance, this component was $v_{z_0}$ for a molecule at a certain initial altitude $z_0$, then at the altitude $z$ the law of conservation of energy holds:

$$\frac{mv_{z_0}^2}{2} = \frac{mv_z^2}{2} + mgz \tag{1.47}$$

where $v_z$ is the value of the $z$-component of the velocity at the altitude $z$. It is clear that the molecules whose kinetic energy $mv_{z_0}^2/2 \leqslant mgz$ cannot rise to an altitude greater than $z$. The highest point $z$ to which these molecules can rise is determined by the equation $z = v_{z_0}^2/2g$. At this altitude, the value of $v_z$ for these molecules becomes equal to zero after which they fall with acceleration like any body thrown vertically upward.

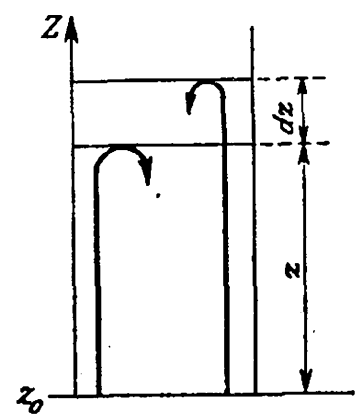


Fig. 10

Let us separate at an arbitrary altitude $z$ a layer of gas having a depth of $dz$ with a base area equal to unity (Fig. 10). The gas in this layer consists of moving molecules. The latter are molecules passing through our layer upward or downward (remember that we are interested only in the components of the velocities of molecules directed along the $Z$-axis). The difference between the upward-bound and downward-bound molecules consists in that the former have $z$-components of their velocities whose modulus without fail exceeds the value $\sqrt{2gz}$ whereas the downward-bound molecules may have $z$-components of their velocities of any values, from zero to infinity.

In conditions of equilibrium, when the number of molecules in the layer should be constant, the number of downward-bound and upward-bound molecules should be equal.

At the altitude $z_0$, the number of molecules in a unit volume having $z$-components of their velocities within the interval from $v_{z_0}$ to $v_{z_0} + dv_{z_0}$ is determined by the equation

$$dn_{z_0} = n_{z_0} f(v_{z_0})\, dv_{z_0}$$

During a unit time, our layer at the altitude $z$ will be crossed by $n_{z_0} v_{z_0} f(v_{z_0})\, dv_{z_0}$ such molecules (see p. 23). The total number of upward-bound molecules crossing the layer (we will denote this number by $N_\uparrow$) is

$$N_\uparrow = \int\limits_{\sqrt{2gz}}^{\infty} n_{z_0} v_{z_0} f(v_{z_0})\, dv_{z_0} = n_{z_0} \int\limits_{\sqrt{2gz}}^{\infty} v_{z_0} f(v_{z_0})\, dv_{z_0}$$

In the same way, we find that the number of downward-bound molecules crossing the layer ($N_\downarrow$) is

$$N_\downarrow = \int\limits_0^{\infty} n_z v_z f(v_z)\, dv_z = n_z \int\limits_0^{\infty} v_z f(v_z)\, dv_z$$

As indicated above, in equilibrium we have $N_\uparrow = N_\downarrow$, i.e.

$$n_{z_0} \int\limits_{\sqrt{2gz}}^{\infty} v_{z_0} f(v_{z_0})\, dv_{z_0} = n_z \int\limits_0^{\infty} v_z f(v_z)\, dv_z \tag{1.48}$$

Dividing both sides of Eq. (1.48) by $n_{z_0}$ and bearing in mind that according to the barometric formula $\frac{n_z}{n_{z_0}} = \exp\left(-\frac{mgz}{kT}\right)$, we get

$$\int\limits_{\sqrt{2gz}}^{\infty} v_{z_0} f(v_{z_0})\, dv_{z_0} = \exp\left(-\frac{mgz}{kT}\right) \int\limits_0^{\infty} v_z f(v_z)\, dv_z \tag{1.49}$$

From the law of conservation of energy [Eq. (1.47)], we get by differentiation (bearing in mind that the value of $z$ is fixed):

$$v_{z_0}\, dv_{z_0} = v_z\, dv_z$$

We substitute $v_z\, dv_z$ for $v_{z_0}\, dv_{z_0}$ under the integral sign in the left-hand side of Eq. (1.49). The lower limit of integration will now be zero so that

$$\int\limits_0^{\infty} v_z f(v_{z_0})\, dv_z = \exp\left(-\frac{mgz}{kT}\right) \int\limits_0^{\infty} v_z f(v_z)\, dv_z$$

Hence it follows that $f(v_{z_0}) = f(v_z) \exp\left(-\frac{mgz}{kT}\right)$, or

$$f(v_z) = f(v_{z_0}) \exp\left(\frac{mgz}{kT}\right) \tag{1.50}$$

With a view to the equation of the law of conservation of energy (1.47), it is not difficult to see that Eq. (1.50) can hold only if

$$f(v_z) = A \exp\left(-\frac{mv_z^2}{2kT}\right) \quad \text{and} \quad f(v_{z_0}) = A \exp\left(-\frac{mv_{z_0}^2}{2kT}\right)$$

where $A$ is a constant. To become convinced that this is true, it is sufficient for us to introduce these functions into Eq. (1.50), taking account of Eq. (1.47). At any other form of the distribution function, Eq. (1.50) will not be compatible with the law of conservation of energy.

Thus, the function of the distribution of molecules by velocity components along the $Z$-axis has the form

$$f(v_z) = A \exp\left(-\frac{mv_z^2}{2kT}\right) \tag{1.51}$$

The number of molecules in a unit volume whose $z$-components are within the interval from $v_z$ to $v_z + dv_z$ is now expressed by the equation

$$dn = nA \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z \quad \text{or} \quad \frac{dn}{n} = A \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z$$

As already indicated, $dn/n$ is the probability of the fact that the $z$-component of the velocity of any molecule of a gas equals $v_z$ with an accuracy up to $dv_z$.

It remains for us to determine the constant $A$ in the distribution function. For this purpose, it is sufficient to integrate $dn/n$ with respect to all possible values of $v_z$ from $-\infty$ to $+\infty$*. This will give us the probability of the fact that a molecule of the gas has a velocity with some value of the $z$-component. And this probability equals unity because we can say authentically

---

* The possible velocities of molecules do not naturally extend from $-\infty$ to $+\infty$. The natural limit of the velocities of molecules is in any case the velocity of light ($3 \times 10^8$ m/s). It may therefore seem that integration of the function $\exp(-mv_z^2/2kT)$ within the limits from $-\infty$ to $+\infty$ is erroneous.

Actually, the adoption of exactly these limits of integration does not result in an error. The explanation is that the function $\exp(-mv_z^2/2kT)$ diminishes very rapidly with increasing $v_z$. Thus, even at comparatively small values of $v_z$ for which $mv_z^2/2kT \approx 5$, the value of this function is about 1% of its value at $v_z = 0$, when it equals unity.

about any molecule that it has some $z$-component of the velocity (the value of $v_z = 0$ is not worse in any way than every other value!). Thus,

$$\int_{-\infty}^{\infty} \frac{dn}{n} = A \int_{-\infty}^{\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z = 1$$

whence

$$A = \left[ \int_{-\infty}^{\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z \right]^{-1}$$

We introduce a new variable to calculate this integral: $x^2 = mv_z^2/2kT$. Thus,

$$v_z = \sqrt{\frac{2kT}{m}}\, x \quad \text{and} \quad dv_z = \sqrt{\frac{2kT}{m}}\, dx$$

Hence,

$$\int_{-\infty}^{\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z = \sqrt{\frac{2kT}{m}} \int_{-\infty}^{\infty} \exp(-x^2)\, dx$$

It is known that $\int_{-\infty}^{\infty} \exp(-x^2)\, dx = \sqrt{\pi}$. Therefore,

$$\int_{-\infty}^{\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z = \sqrt{\frac{2\pi kT}{m}}$$

The constant $A$ in Eq. (1.51) which interests us is

$$A = \left(\frac{m}{2\pi kT}\right)^{1/2}$$

The expression for the distribution function becomes

$$f(v_z) = \frac{dn}{n\, dv_z} = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_z^2}{2kT}\right) =$$

$$= \pi^{-1/2} \left(\frac{m}{2kT}\right)^{1/2} \exp\left(-\frac{mv_z^2}{2kT}\right) \tag{1.52}$$

This function or, to be more exact, Eq. (1.51) has the form depicted in Fig. 11. A glance at the graph in this figure shows that the function $f(v_z)$ tends to zero when $v_z \to \infty$. But the fraction of molecules with the $z$-component of the velocity equal to zero does not equal zero. Inspection

of Eq. (1.51) and the curve in Fig. 11 shows that the fraction of molecules whose $z$-components of their velocities are close to zero equals $A$ (and this is exactly the physical meaning of the constant). The fraction of such molecules diminishes with increasing temperature.

We have obtained the distribution function of molecules by velocity components upon considering a gas in the field of the force of gravity. We must remind our readers that this does not at all mean that the form of the molecule distribution by velocity components is connected in some way or other with the action of the force of gravity, or that it is precisely the force of gravity that creates this distribution. We have already noted that the barometric formula, which we used in our derivation, is itself a result of the velocity distribution of molecules. The part played by the force of gravity in our derivation consisted only in that it "developed" the distribution existing in the gas. That the force of gravity plays no part in establishing the distribution is already obvious from the fact that the distribution function does not include the quantity $g$ characterizing the force of gravity.

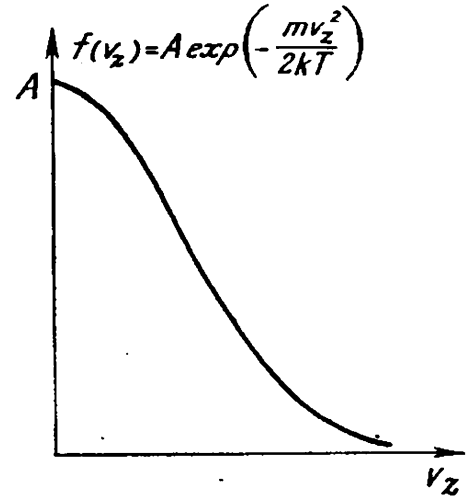



Fig. 11

## 1.13. DISTRIBUTION OF MOLECULES BY VELOCITIES

The expression we have just obtained for the distribution function of the molecules of a gas by the $z$-components of the velocities, i.e.

$$\frac{dn_z}{n\,dv_z} = A\exp\left(-\frac{mv_z^2}{2kT}\right)$$

cannot be the "privilege" of only the $z$-component. Exactly the same expressions should also determine the distribution of the molecules for the other velocity components, and we get

$$\frac{dn_x}{n\,dv_x} = A\exp\left(-\frac{mv_x^2}{2kT}\right) \quad \text{and} \quad \frac{dn_y}{n\,dv_y} = A\exp\left(-\frac{mv_y^2}{2kT}\right)$$

Now we can find the probability of the fact that the velocity of a molecule simultaneously complies with three conditions:

(1) its component along the $X$-axis is within the limits from $v_x$ to $v_x + dv_x$;
(2) its component along the $Y$-axis is within the limits from $v_y$ to $v_y + dv_y$;
(3) its component along the $Z$-axis is within the limits from $v_z$ to $v_z + dv_z$.

The values of the velocity components along each of the coordinate axes do not depend on the values of the components along the other axes.

Hence, the probability of the velocity of a molecule simultaneously complying with all three of the above conditions is the probability of a complex "event". And the latter equals the product of the probabilities of each event considered separately. If we let $dn_{xyz}$ stand for the number of molecules in a unit volume of a gas whose velocity components along the axes of coordinates are within the limits indicated above, we can write

$$\frac{dn_{xyz}}{n} = A^3 \exp\left(-\frac{mv^2}{2kT}\right) dv_x\, dv_y\, dv_z$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$. Hence,

$$dn_{xyz} = nA^3 \exp\left(-\frac{mv^2}{2kT}\right) dv_x\, dv_y\, dv_z$$

or

$$dn_{xyz} = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv_x\, dv_y\, dv_z \qquad (1.53)$$

This equation shows how many molecules from among those in a unit volume of a gas have velocities whose components along the axes of coordinates are in the intervals between $v_x$ and $v_x + dv_x$, $v_y$ and $v_y + dv_y$, and $v_z$ and $v_z + dv_z$, i.e. have a velocity that is within an interval specified in both magnitude and direction. This equation can be given an illustrative geometrical interpretation.

Assume that we have gathered all the molecules in a unit volume of a gas whose components of the velocity $v$ are confined within the intervals indicated above, and have released them. In one second, all of them will be at a distance $v$ from their initial position in a parallelepiped having sides of $dv_x$, $dv_y$, and $dv_z$, i.e. in the volume $d\omega = dv_x\, dv_y\, dv_z$. This is shown in Fig. 12 where our mental experiment is depicted in a special system of coordinates along whose axes the components $v_x$, $v_y$, and $v_z$ are laid off. The number of molecules related to a unit volume of this parallelepiped (do not confuse it with the number of molecules in a unit volume of the gas; here we are speaking of a unit volume in the "space" of the velocities), by Eq. (1.53), is

$$\frac{dn_{xyz}}{d\omega} = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right)$$

This quantity cannot naturally depend on the direction of the velocity vector $\boldsymbol{v}$. It is therefore a simple matter now to also find the function of the distribution of molecules by velocities independently of their direction. Indeed, if we get together all the molecules in a unit volume of a gas whose velocities are within the interval from $v$ to $v + dv$ in all directions and release them, they will fly apart in all directions. In one second, they will be uniformly distributed in a spherical layer with a thickness of $dv$

and a radius of $v$ (Fig. 13). This spherical layer is composed of the "parallelepipeds" mentioned above. The number of molecules in a unit volume of this layer (again, it should not be confused with the number of molecules in a unit volume of the gas) is the same as in each parallelepiped, i.e. is

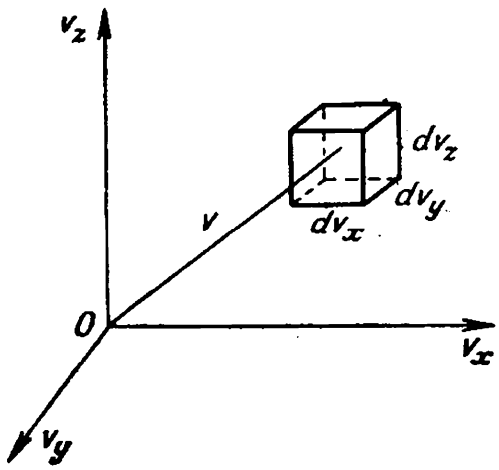



Fig. 12

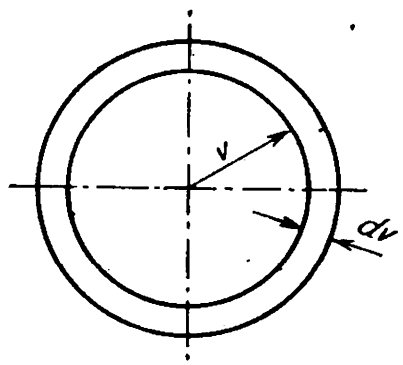



Fig. 13

determined by Eq. (1.53). The number of molecules in the *entire* layer is exactly the number of molecules in a unit volume of the gas whose velocities are within the interval from $v$ to $v + dv$.

This number is

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) d\Omega$$

where $d\Omega$ is the volume of the spherical layer, equal to $4\pi v^2\, dv$. Thus,

$$dn = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv =$$

$$= 4n\pi^{-1/2}\left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

or

$$\frac{dn}{n} = 4\pi^{-1/2}\left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv \qquad (1.54)$$

This equation expresses the *Maxwell distribution law for the velocities of molecules*.

The quantity $dn/n$ is the probability of the fact that the velocity of an arbitrarily chosen molecule of the gas will be within the interval between $v$ and $v + dv$. In other words, $dn/n$ is the fraction of all the molecules in a unit volume whose velocities are within the interval from $v$ to $v + dv$.

The quantity

$$f(v) = \frac{dn}{n\,dv} = 4\pi^{-1/2}\left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \qquad (1.55)$$

is the *distribution function* of molecules by velocities. It determines the fraction of molecules in a unit volume of a gas whose velocities are within an interval of velocities equal to unity and including a specified velocity.

A graphical view of the Maxwell distribution function is shown in Fig. 14. As should be expected, it becomes equal to zero at $v = 0$ and $v \to \infty$

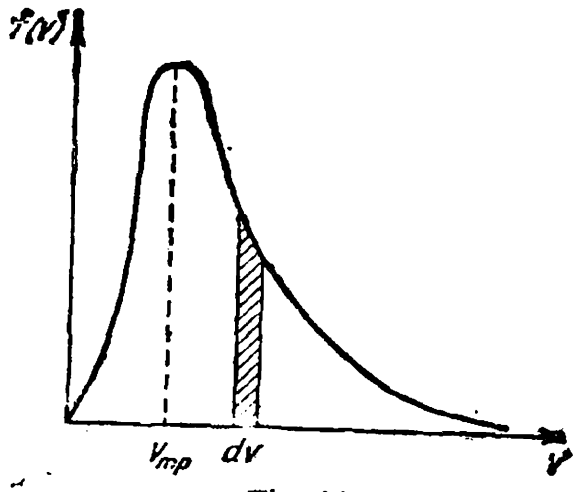



Fig. 14

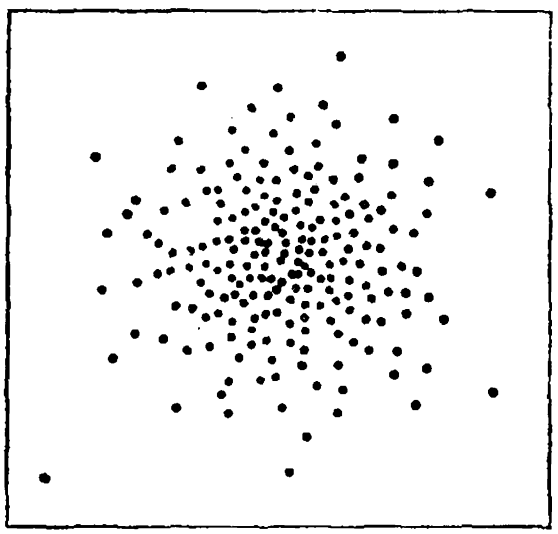


Fig. 15

because a gas has no stationary molecules and no molecules having infinitely great velocities. It can be seen from the curve in Fig. 14 that the distribution function has a maximum at a certain value of the velocity $v_{mp}$. This means that the greatest fraction of all the gas molecules travel with velocities whose values are close to $v_{mp}$. We can also say that velocities close to $v_{mp}$ are encountered in the molecules of the gas more often than others, i.e. that the probability of the fact that the velocity of a molecule is close to $v_{mp}$ is the greatest. Hence, the velocity $v_{mp}$ which the maximum of the Maxwell distribution curve corresponds to is called the *most probable* velocity.

To gain a better understanding of the difference between the distribution by *velocities* and the distribution by *velocity components*, let us consider the analogy between our case and another process in which the main part is also played by laws of chance.

Imagine shooting at a target on which the bull's-eye is a point at its centre. No matter how skilled the marksman is and how perfect his arms are, the bullets will not hit the bull's-eye exactly, but will reach the target close to it and at different distances from it (Fig. 15). This is explained by various factors that cannot be taken into account by the marksman: not exactly identical charges in a cartridge, the influence of gusts of wind, etc. (when dealing with a gas, these random factors include collisions

between the molecules, which will be dealt with below). With a sufficiently great number of shots, the distribution of the bullets around the bull's-eye, i.e. the distribution according to distances from it, will be found to obey a quite definite law. It is a simple matter to find the nature of this law. Figure 15 shows the distribution of the hits around the bull's-eye. This distribution can be assessed in two ways.

We can divide the entire area of the target into circular bands (Fig. 16) as is done in shooting contests by drawing a number of circles at equal distances $\Delta r$ from one another and determine the number of hits $\Delta n$ in each band, i.e. the number of hits at the given distance $r$ from the bull's-eye within the interval from $r$ to $r + \Delta r$. In this case, the number of hits in the central circle, if it is sufficiently small, will be close to zero because it is impossible to hit such a small circle. With an increase in the distance from the centre to a circular band, the number of hits in it will first grow, next reach a maximum, then diminish, and at a considerable distance from the bull's-eye it will become equal to zero (see the curve in Fig. 16).

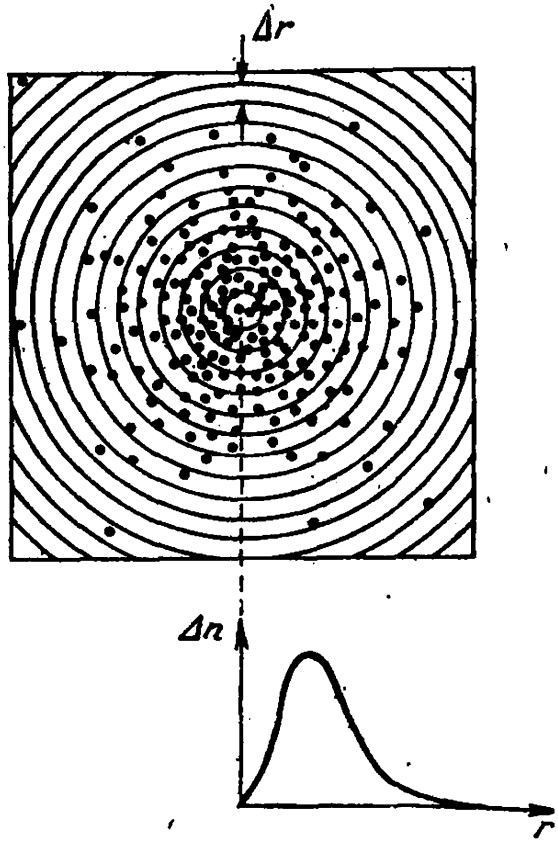



Fig. 16

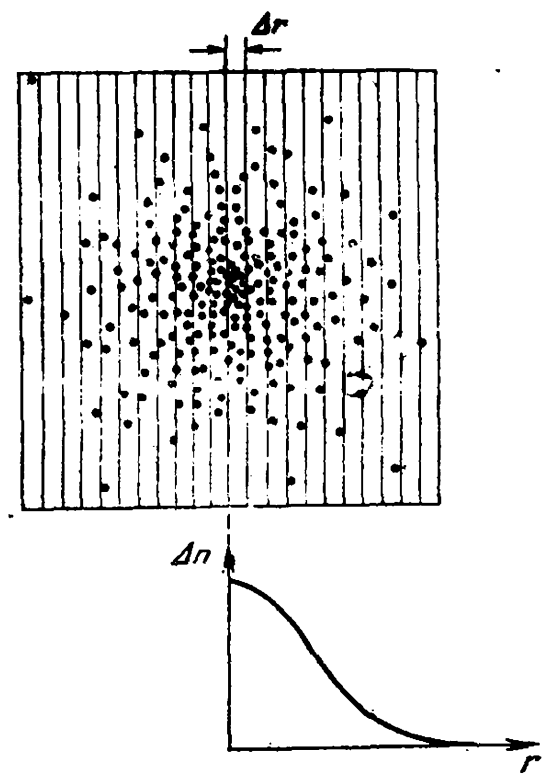



Fig. 17

We can proceed in a different wai. We divide the area of the target into strips by conducting a number of par allel straight lines that are at the same distance $\Delta r$ from one another (Fig. 17). If we now determine the number of hits $\Delta n$ falling to the share of each strip, it will befound to monotonously diminish with a growing distance from the central strip as can readily be seen from Fig. 17. At a sufficiently great distance from the bull's-eye,

this number tends to zero. This is illustrated by the curve in Fig. 17, similar to that in Fig. 11.

The first of the two methods of describing the distribution corresponds to determination of the function $f(v)$, the second — to determination of the distribution $f(v_x)$ by velocity components.

By using a velocity distribution curve, we can graphically find the fraction of the molecules $dn/n$ in a unit volume of a gas whose velocities are within a given interval of velocities $dv$. It equals the area of the hatched strip in Fig. 14 with the base $dv$ and the height $f(v)$. The entire area between the distribution curve and the velocity axis gives us the total number of molecules in a unit volume.

Inspection of Eq. (1.55) shows that the shape of the distribution curve depends on the nature of the gas (the equation includes the mass $m$ of a molecule) and the temperature. Figure 18 shows curves of the distribution of nitrogen molecules by velocities at different temperatures. It can be seen from these curves that elevation of the temperature is attended by a growth in the velocities of the molecules so that the entire curve is displaced in the direction of greater velocities. But the areas between the curves and the velocity axis remain unchanged. As a result, the peak of the curve lowers for a higher temperature.

In deriving the equation of the Maxwellian distribution of molecules by velocities, we disregarded the collisions between molecules, although the latter cannot fail to affect the velocities of the molecules and, consequently, their distribution by velocities. Actually, the collisions are what makes the Maxwellian distribution by velocities set in. Indeed, assume that a gas is in a state such that all its molecules have identical (in modulus) velocities. This state cannot be stable (equilibrium) because collisions between molecules will inevitably result in their velocities no longer being the same. Each time two molecules collide, the velocity of one of them grows and of the other diminishes. And J. Maxwell was the first to pay attention to the fact that such a state must exist in which the number of molecules whose velocity increases upon collisions equals the number of molecules whose velocity decreases as a result of the collisions. It is exactly this state that is the equilibrium one. The Maxwellian velocity distribution law corresponds to this state. L. Boltzmann later showed that if a gas is in a state when the velocity distribution of its molecules does not obey the Maxwellian distribution law, this gas owing to collisions between its molecules will spontaneously pass over to a state with the Maxwellian distribution.

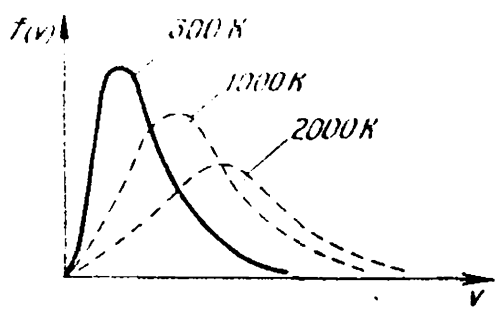



Fig. 18

The Maxwellian distribution (sometimes called the Maxwell-Boltzmann distribution) is an *equilibrium* distribution. This was the starting point of our discussion. Consequently, for instance in deriving Eq. (1.51), we had no need to take collisions into account. If some of the molecules that had left the layer $\Delta z_0$ did not reach the layer $\Delta z$ owing to collisions, there were some other molecules that did reach it as a result of collisions although they were not supposed to.

We have always called the molecular movements occurring in a gas chaotic or random. Now we can give an exact definition of the concept of the random nature of thermal motion: *the motion of molecules is completely random* (chaotic) *if the velocities of the molecules are distributed according to the Maxwell law.*

Molecules perform such completely random movements when a gas is in a state of equilibrium. We have seen in Sec. 1.3 that this state is characterized by the magnitude of the temperature. The latter, in turn, is determined by the mean kinetic energy of molecular motion. Hence it follows that the mean kinetic energy of exactly the *chaotic* movements determines the temperature. Any directed motion of the molecules, however, no matter what their velocities are in such motion, has no relation to temperature. No matter how great is the velocity of the air forming a strong wind, it does not make it hot. Even the strongest winds may be either warm or cold because the temperature of a gas is determined not by the directed velocity of the wind, but by the random movements which the molecules perform in addition to the directed motion of the gas as a whole and independently of it.

## 1.14. MEAN VELOCITIES OF MOLECULES

Using the Maxwell distribution function, we can calculate a number of quantities that are important for molecular physics. As examples, we shall give the calculation of the arithmetic mean velocity $\bar{v}$, the mean square velocity $\overline{v} = \sqrt{\overline{v^2}}$, which we have already calculated on an earlier page (see Sec. 1.6), and, finally, the most probable velocity $v_{mp}$. We shall begin with the arithmetic mean velocity of molecules.

*Arithmetic Mean Velocity of Molecules.* The arithmetic mean velocity $\bar{v}$ by definition equals the ratio of the sum of all the velocities of all the molecules in a unit volume to the number of molecules in the unit volume.

The number of molecules in a unit volume whose velocities are within the interval from $v$ to $v + dv$ is $nf(v)\,dv$. The sum of the velocities of all such molecules equals $vnf(v)\,dv$. To find the sum of the velocities of all the molecules having any velocities, we must integrate this function with

respect to all possible velocities from zero to infinity. Hence, the sum of all the velocities is

$$\int_0^\infty vn f(v)\, dv$$

and the arithmetic mean velocity $\bar{v}$ is

$$\bar{v} = \frac{1}{n} \int_0^\infty vn\, f(v)\, dv = \int_0^\infty v f(v)\, dv \tag{1.56}$$

Using the previously obtained Eq. (1.55) for $f(v)$ in Eq. (1.56), we get

$$\bar{v} = 4\pi^{-1/2} \left(\frac{m}{2kT}\right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv \tag{1.57}$$

To calculate the integral in this equation, we transform the integrand:

$$v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv = v^2 \exp\left(-\frac{mv^2}{2kT}\right) v\, dv$$

Since $v\, dv = \frac{1}{2}\, d(v^2)$, then

$$v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv = \frac{1}{2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) d(v^2)$$

and

$$\bar{v} = 4\pi^{-1/2} \left(\frac{m}{2kT}\right)^{3/2} \frac{1}{2} \int_0^\infty v^2 \exp\left(-\frac{mv^2}{2kT}\right) d(v^2)$$

Introducing the new variable $z = mv^2/2kT$, we get

$$\frac{1}{2} \int_0^\infty v^2 \exp\left(-\frac{mv^2}{2kT}\right) d(v^2) = \frac{1}{2} \left(\frac{2kT}{m}\right)^2 \int_0^\infty z\, e^{-z}\, dz$$

Integration by parts gives

$$\int_0^\infty z\, e^{-z}\, dz = 1$$

Thus, for the integral in Eq. (1.57), we get the expression:

$$\int_0^\infty v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv = 2\left(\frac{kT}{m}\right)^2$$

Inserting it into Eq. (1.57), we find the following expression for $\bar{v}$:

$$\bar{v} = 4\pi^{-1/2}\left(\frac{m}{2kT}\right)^{3/2} 2\left(\frac{kT}{m}\right)^2 = \sqrt{\frac{8kT}{\pi m}} \tag{1.58}$$

In a similar way, we can also calculate the arithmetic mean value of a *velocity component* along any coordinate axis.

Strictly speaking, the mean value of any velocity component equals zero because it may be either positive or negative with equal probability. But this cannot be said of the mean value of the *modulus* of such a component. Let us find, for example, the arithmetic mean value of the modulus of the $x$-component of the velocity, i.e. the quantity $\overline{|v_x|}$. We can write an equation for it similar to Eq. (1.56):

$$\overline{|v_x|} = \int_{-\infty}^{\infty} v_x f(v_x)\, dv_x \tag{1.59}$$

Here $f(v_x)$ is the distribution function of the molecules with respect to the component $v_x$ which we found earlier:

$$f(v_x) = \pi^{-1/2}\left(\frac{m}{2kT}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2kT}\right)$$

Introducing this expression into Eq. (1.59), we get

$$\overline{|v_x|} = \pi^{-1/2}\left(\frac{m}{2kT}\right)^{1/2} \int_{-\infty}^{\infty} v_x \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x$$

The integral in this equation is taken with the aid of substitution of the variable $mv_x^2/2kT \equiv z^2$. Hence, for $\overline{|v_x|}$ we get the expression

$$\overline{|v_x|} = \sqrt{\frac{2kT}{\pi m}} \tag{1.60}$$

Comparing Eqs. (1.58) and (1.60), we see that the mean value of the modulus of the $x$-component $\overline{|v_x|}$ is one-half of the mean value of the velocity $v$:

$$\overline{|v_x|} = \frac{v}{2}$$

This expression makes it possible to solve the interesting problem of the mean number of impacts of molecules against a unit wall area of a vessel in a unit time.

We have seen in Sec. 1.2 that the number of molecules intersecting the area $A$ during the time $\Delta t$ equals $\frac{1}{2} n v_x A \Delta t$. Hence it follows that $\frac{1}{2} n v_x$ molecules strike a *unit* area in a *unit* time. Substituting here for $v_x$ its mean value $\overline{|v_x|}$, we find that the mean number of collisions $\bar{\nu}$ of the molecules against a unit area in a unit time is

$$\bar{\nu} = \frac{1}{2} n \overline{|v_x|} = \frac{n\bar{v}}{4}$$

*Mean Square Velocity of Molecules.* To find the mean square (or effective) velocity of molecules $\sqrt{\overline{v^2}}$, we must calculate the ratio between the sum of the squares of the velocities of the molecules in a unit volume and the number of molecules in this volume. Repeating our previous reasoning, we get

$$\overline{v^2} = \int_0^\infty v^2 f(v)\, dv$$

Using here Eq. (1.55) for $f(v)$, we get

$$\overline{v^2} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

We find the integral in this equation by integrating by parts, and get

$$\int_0^\infty v^4 \exp\left(-\frac{mv^2}{2kT}\right) dv = \frac{3}{8} \left(\frac{2kT}{m}\right)^{5/2} \sqrt{\pi}$$

Hence,

$$\overline{v^2} = \frac{3kT}{m} \quad \text{and} \quad \bar{v} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \tag{1.61}$$

We have obtained such an equation in a previous section.

## 1.15. THE MOST PROBABLE VELOCITY OF MOLECULES

We shall now calculate the most probable velocity $v_{\text{mp}}$ of molecules — the velocity near which the velocities of the greatest number of molecules of a gas group themselves. The maximum on the Maxwell distribution curve

corresponds to this velocity (see Fig. 14). Consequently, to find the velocity $v_{mp}$, we must equate the derivative of the distribution function (1.55) to zero:

$$\frac{d}{dv} f(v) = \frac{d}{dv}\left[4\pi^{-1/2}\left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)\right]$$

This equation will be obeyed if

$$\frac{d}{dv}\left[v^2 \exp\left(-\frac{mv^2}{2kT}\right)\right] = 0$$

Differentiation yields

$$2v \exp\left(-\frac{mv^2}{2kT}\right)\left(1 - \frac{mv^2}{2kT}\right) = 0$$

This equation is observed either when $v = 0$, or when $v = \infty$, or when $1 - \frac{mv^2}{2kT} = 0$. It is clear that the first two conditions do not correspond to the maximum on the distribution curve. Hence, the value of $v_{mp}$ is determined from the condition that

$$1 - \frac{mv_{mp}^2}{2kT} = 0$$

whence

$$v_{mp} = \sqrt{\frac{2kT}{m}} \tag{1.62}$$

By comparing Eqs. (1.58), (1.61), and (1.62), we find the relationship between the three calculated values of the velocities:

$$\bar{\bar{v}} = \sqrt{\frac{3\pi}{8}}\,\bar{v} = 1.09\bar{v} = \sqrt{\frac{3}{2}}\,v_{mp} = 1.22v_{mp}$$

It can be seen that the difference between these three values is not very great — both the arithmetic mean and the mean square velocities are close to the most probable velocity.

## 1.16. THE MAXWELL EQUATION FOR RELATIVE VELOCITIES

To solve many problems, it is convenient to use the Maxwell equation in the form that is obtained if we express the velocities of molecules not in conventional units, but in relative ones, taking the most probable velocity of the molecules $v_{mp}$ as the unit of velocity. The relative velocity $u$ will therefore be

$$u = \frac{v}{v_{mp}}$$

where $v$ = preset velocity of the molecules
$v_{mp}$ = most probable velocity at a given temperature.
We have already established [see Eq. (1.62)] that

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

The Maxwell equation

$$\frac{dn}{n\,dv} = 4\pi^{-1/2}\left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)$$

contains the expression $m/2kT$ two times. Substituting for it the expression $1/v_{mp}^2$ equal to it and denoting $v/v_{mp}$ by the letter $u$, we can give the Maxwell equation the following form:

$$\frac{dn}{n\,du} = 4\pi^{-1/2}\,u^2\,e^{-u^2} \tag{1.63}$$

This equation is universal. In this form, the distribution function depends neither on the kind of gas nor on the temperature.

A similar equation can be derived for the function of the distribution of molecules by velocity components along the axes of coordinates. If we are dealing with the $x$-component of the velocity, then by introducing here the relative velocity $u_x = v_x/v_{mp}$, we can write distribution function (1.52) in the form

$$\frac{dn}{n\,du_x} = \pi^{-1/2}\,e^{-u_x^2} \tag{1.64}$$

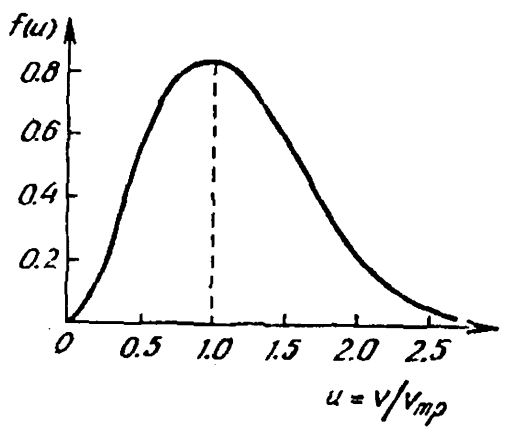



Fig. 19

To solve various problems connected with the distribution of molecules by velocities, it is convenient to use the equations of the distribution functions in the form of Eqs. (1.63) and (1.64). Figure 19 shows a distribution curve for the relative velocities.

The functions $4\pi^{-1/2}u^2e^{-u^2}$ and $\pi^{-1/2}e^{-u_x^2}$ can be calculated beforehand for various values of $u$ and $u_x$ and presented in the form of graphs. The latter can be used to determine the required values. Table 1 gives the values of these functions calculated with an accuracy that is sufficient for solving many problems.

Suppose, for example, we have to find the fraction of nitrogen particles at room temperature (300 K) whose velocities are between 275 and 276 m/s.

*Table 1*

| $u$, $u_x$ | $f(u)=4\pi^{-1/2}u^2e^{-u^2}$ | $f(u_x)=\pi^{-1/2}e^{-u_x^2}$ | $u$, $u_x$ | $f(u)=4\pi^{-1/2}u^2e^{-u^2}$ | $f(u_x)=\pi^{-1/2}e^{-u_x^2}$ |
|---|---|---|---|---|---|
| 0.1 | 0.022 | 0.558 | 1.2 | 0.770 | 0.133 |
| 0.2 | 0.087 | 0.542 | 1.3 | 0.703 | 0.104 |
| 0.3 | 0.185 | 0.515 | 1.4 | 0.623 | 0.079 |
| 0.4 | 0.308 | 0.480 | 1.5 | 0.535 | 0.059 |
| 0.5 | 0.439 | 0.439 | 1.6 | 0.447 | 0.044 |
| 0.6 | 0.567 | 0.393 | 1.7 | 0.362 | 0.031 |
| 0.7 | 0.677 | 0.345 | 1.8 | 0.286 | 0.022 |
| 0.8 | 0.761 | 0.297 | 2.0 | 0.165 | 0.010 |
| 0.9 | 0.813 | 0.251 | 2.2 | 0.086 | 0.004 |
| 1.0 | 0.830 | 0.208 | 2.4 | 0.041 | 0.002 |
| 1.1 | 0.814 | 0.168 | 3.0 | 0.003 | — |

First we find the most probable velocity:

$$v_{mp}=\sqrt{\frac{2kT}{m}}=\sqrt{\frac{2RT}{\mu}}=\sqrt{\frac{2\times 8.31\times 10^3\times 3\times 10^2}{28}}\approx 394 \text{ m/s}$$

The relative velocity $u$ is

$$u=\frac{v}{v_{mp}}=\frac{275}{394}\approx 0.70$$

It follows from the expression $u=v/v_{mp}$ that $du=dv/v_{mp}$. In the given case, the velocity interval of 1 m/s is sufficiently small, and it may be considered that $du=\Delta v/v_{mp}=0.0025$. Using Table 1 (or, if interpolation is necessary, a graph which it is quite simple to construct according to the data of Table 1), we find that for a relative velocity of $u=0.70$ the value of the function $f(u)$ is

$$f(u)=\frac{dn}{n\,du}=4\pi^{-1/2}u^2e^{-u^2}=0.677$$

whence

$$\frac{dn}{n}=0.677\times 0.0025=1.7\times 10^{-3}$$

Hence, only 0.17% of all the molecules have velocities within the given interval.

An interesting problem connected with the distribution of molecules by velocities is the determination of the fraction of all the molecules whose velocities exceed a specified value. To solve such problems, it is also con-

venient to use the Maxwell equation for the relative velocities, i.e. the equation

$$\frac{dn}{n} = 4\pi^{-1/2}u^2e^{-u^2}\,du$$

If we are to find the fraction of molecules whose velocities exceed a certain specified value $v$, and, consequently, a definite $u$, the above equation must be integrated within the limits from the given value of $u$ to infinity, so that

$$\frac{n_{>u}}{n} = 4\pi^{-1/2}\int_u^\infty z^2 e^{-z^2}\,dz \qquad (1.65)$$

where $n_{>u}$ is the number of molecules whose relative velocities are greater than the specified $u$. Therefore, solution of the problem consists in calculating the integral in Eq. (1.65). Table 2 gives its values for different values of $u$. Examination of the table shows that the number of molecules whose

*Table 2*

| $u$ | $4\pi^{-1/2}\int_u^\infty z^2e^{-z^2}\,dz$ | $u$ | $4\pi^{-1/2}\int_u^\infty z^2e^{-z^2}\,dz$ | $u$ | $4\pi^{-1/2}\int_u^\infty z^2e^{-z^2}\,dz$ |
|---|---|---|---|---|---|
| 0.1 | 0.9992 | 0.8 | 0.7340 | 1.5 | 0.2123 |
| 0.2 | 0.9941 | 0.9 | 0.6550 | 1.6 | 0.1632 |
| 0.3 | 0.9807 | 1.0 | 0.5724 | 1.7 | 0.1230 |
| 0.4 | 0.9582 | 1.1 | 0.4900 | 1.8 | 0.0905 |
| 0.5 | 0.9190 | 1.2 | 0.4105 | 1.9 | 0.0602 |
| 0.6 | 0.8685 | 1.3 | 0.3370 | 2.0 | 0.0460 |
| 0.7 | 0.8061 | 1.4 | 0.2702 | | |

velocities exceed the most probable value, i.e. the molecules for which $v > v_{mp}$, is 57.24% of all the molecules in a gas — more than one-half. This means that the Maxwell distribution curve is not symmetrical relative to the maximum, which can also be seen quite clearly from the graphs in Figs. 14, 18, and 19.

### 1.17. VELOCITY DISTRIBUTION LAW FOR GAS MOLECULES AND PLANETS' ATMOSPHERES

We have already drawn our readers' attention to the fact that the Earth's atmosphere cannot be in a completely equilibrium state, and that the continuous dissipation of air into outer space should take place (p. 54).

The law of distribution of molecules by velocities permits us to consider this problem in greater detail.

For a body to overcome the Earth's attraction and leave it, it must have the so-called second-cosmic or escape velocity equal to $1.12 \times 10^4$ m/s. At this velocity, it will have the kinetic energy adequate for performing the work which is needed to remove it to infinity. This also relates to molecules of the air in the Earth's atmosphere to an equal extent.

According to the Maxwell distribution law, the atmosphere contains molecules whose velocities exceed the escape velocity. It is quite clear that such molecules (and only such) leave the atmosphere and become dissipated in outer space.

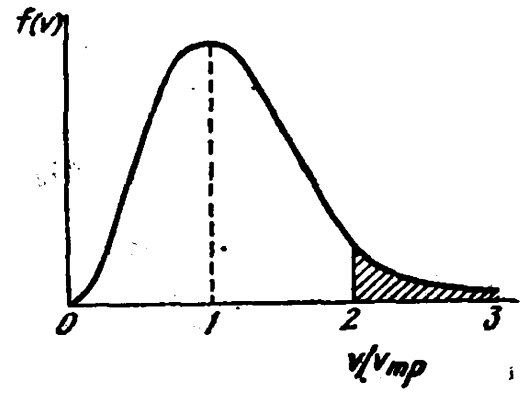


Fig. 20

The equation of the distribution of molecules by velocities permits us to find the fraction of such molecules in the air of the Earth's atmosphere. It is simpler to do this graphically. Figure 20 shows a Maxwell distribution curve. The velocities are laid off along the axis of abscissas in relative units $v/v_{mp}$ (see Sec. 1.16) so that unity on this axis corresponds to the maximum of the curve (the most probable velocity). At 0 °C, the most probable velocity is $3.94 \times 10^3$ m/s. Hence,

$$\frac{1.12 \times 10^4}{3.94 \times 10^3} = 28$$

i.e. the escape velocity is 28 times greater than the most probable velocity. Consequently, in Fig. 20, an abscissa of 28 corresponds to the escape velocity. We can see from the shape of the curve without any calculations how negligible is the fraction of particles in the atmosphere having a velocity adequate to leave it. For purposes of comparison, in Fig. 20 the area equal to the fraction of particles whose velocities are within $2v_{mp}$ and $3v_{mp}$ is hatched. The fraction of the particles whose velocity exceeds $28v_{mp}$ would be equal to the area to the right of the figure 28 in this diagram.

For the Moon, whose mass and, therefore, whose gravitational attraction are much smaller than those of the Earth, the escape velocity equals $2.4 \times 10^3$ m/s. In the same diagram, an abscissa of 6 corresponds to this velocity. Only a small fraction of all the particles have such a velocity (or a greater one) in this case too, but the fraction is not so small that the Moon could not have virtually completely lost any atmosphere which it may have had already in remote ages.

## 1.18. EXPERIMENTAL VERIFICATION OF DISTRIBUTION LAW

The velocity distribution law was verified experimentally by using the method of molecular beams. We made our acquaintance with this method on a previous page in describing O. Stern's experiment. And this experiment itself with an insignificant alteration of the details can not only give us the values of the velocities of molecules, but also help us to determine the law of their distribution by velocities. If we use glass instead of metal as the target on which the atoms condense, the transparency of the deposit in different portions of the displaced stripe can be used to assess the number of atoms that have reached these portions, and, consequently, their distribution by velocities. Stern did run such an experiment, but the accuracy of measurements he achieved was not adequate.

In 1947, Stern, this time together with J. Easterman and O. Simpson, arranged a somewhat unusual and very difficult experiment for verifying the law of distribution of molecules by velocities. In this experiment, in which the method of molecular beams was also used, the free fall of the molecules of a beam was observed in the field of gravitational attraction. The experiment is shown schematically in Fig. 21.

The source of atoms was molten cesium (the melting point of cesium is 301.65 K, or 28.5 °C) which evaporated from a small furnace $A$ where the cesium was heated to 450 K. The cesium atoms flew out of the furnace through narrow horizontal slot $S_1$ 0.02 mm wide. Second slot $S_2$ having the same width as the first one was placed at a distance of 1 m from $S_1$. Target $D$ in the form of a thin tungsten wire also 0.02 mm thick was placed at a distance of 1 m from slot $S_2$ (the wire is perpendicular to the plane of the drawing). Thus, the total length $L$ of the beam from the source to the target was 2 m. The entire arrangement was placed in a cylinder in which a high vacuum was maintained. Slots $S_1$, $S_2$, and target $D$ were installed along one strictly horizontal straight line.

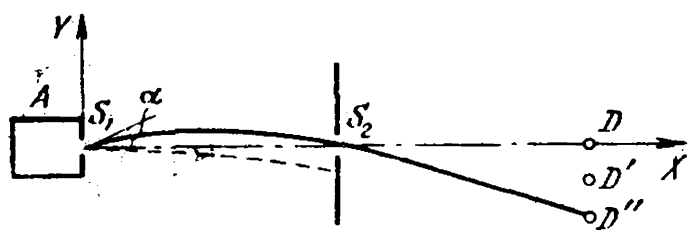



Fig. 21

The atoms hitting the target were counted as follows.

An electric current was passed through the wire-target. This heated the latter to such a high temperature at which the cesium atoms getting onto it became ionized, transforming into positively charged ions. These ions immediately left the target and got onto the negatively charged cylinder surrounding the wire. Slots were made in the cylinder for passage of the atoms. An electric current formed by the ions passed between the wire and

the cylinder, which after amplification could be measured with a high accuracy (this method of registering the atoms of a beam is called the method of surface ionization. It is generally used for easily ionizing atoms, which atoms of the alkali metals relate to). The current was directly determined by the number of ions and, consequently, the number of atoms getting onto the wire.

The cesium atoms in the beam "fell" along their two-metre path from the source to the target under the action of gravitational attraction and travelled along a parabola. Hence, the atoms that emerged from slot $S_1$ with a velocity directed horizontally along the $X$-axis did not pass through slot $S_2$ and did not reach the target (the dash line in Fig. 21). The atoms which emerged from $S_1$ at a certain small angle $\alpha$, as shown in the figure by the solid line, passed through slot $S_2$.

The coordinates $x$ and $y$ of any point of the path of such particles are known to be expressed by the following equations:

$$x = v_x t \quad \text{and} \quad y = v_y t - \frac{gt^2}{2}$$

Eliminating the time from these two equations, we get

$$y = v_y \frac{x}{v_x} - \frac{gx^2}{2v_x^2} \tag{1.66}$$

This is exactly the equation of the parabola along which the atoms travelled.

At the point where the path of the atoms passes through slot $S_2$, we have $y = 0$ and $x = L/2$. Equation (1.66) for this point becomes

$$v_y \frac{L}{2v_x} - \frac{gL^2}{8v_x^2} = 0$$

Hence for the quantity $v_y$, we get the expression

$$v_y = \frac{gL}{4v_x}$$

We are interested in the quantity $y$, i.e. the displacement of the atoms from the $X$-axis at a distance of $x = L$ from the source. Substituting $L$ for $x$ and $gL/4v_x$ for $v_y$ in Eq. (1.66), we have

$$y = -\frac{gL^2}{4v_x^2}$$

Thus, the displacement of the atoms in a vertical direction is determined only by the value of $v_x$, which at small angles $\alpha$ is very close to the value of the velocity $v$ of the atoms itself (because $v_x = v \cos \alpha$, and at small angles $\cos \alpha$ is close to unity). By moving the wire-target in a vertical direction (positions $D'$ and $D''$ in the figure) and measuring the ionic current (i.e. the number of atoms hitting the target) at different heights, we find the number

of atoms having different velocities. This gives us the distribution of the atoms by velocities. It must be noted that by measuring the number of atoms hitting the wire at a definite height, we determine the number of atoms whose velocities are within a certain *interval* of velocities because no matter how small the thickness of the wire is, it is nevertheless finite, and is hit by atoms with close, but not identical, velocities.

The difficulties encountered in running this experiment can be seen from the fact that even the slowest atoms were displaced by a height of only about 0.2 mm (the atoms having the most probable velocity were displaced by 0.174 mm in the experiment conducted by Stern, Easterman, and Simpson). Since the width of slots $S_1$ and $S_2$ and the thickness of the wire-target were only 0.02 mm (the beam had the same thickness!), however, the measurements were nevertheless possible with a sufficiently high accuracy. And not only with cesium atoms, but also with a beam of sodium atoms for which the falling height was still smaller.

The measurements completely confirmed the Maxwell distribution law.

## 1.19. MEASURING PARAMETERS OF STATE

**Measuring Volume.** The volume of a gas equals the volume of the vessel it occupies. Therefore, determination of the volume of a gas consists in measuring the free volume of its vessel.

The simplest way of measuring the volume of a vessel is to fill the volume being measured with a liquid whose density is well known. By weighing the vessel before and after it is filled with the liquid, we find the volume according to the equation

$$V = \frac{M_1 - M_2}{\rho}$$

where $M_1$ and $M_2$ = masses of filled and empty vessel, respectively
$\rho$ = density of the liquid used.

Water or mercury is generally used for filling the vessel. In both cases, corrections must be introduced connected with the fact that these liquids form a meniscus. Special tables have been compiled that give the values of these corrections.

It must be remembered that measurement in the way described above gives the value of the volume of a vessel at the temperature at which weighing was performed. If the vessel is used at another temperature, corrections must be introduced for thermal expansion or contraction of the material of the vessel.

It is often impossible to weigh a vessel and fill it with a liquid for measuring its volume (this relates in particular to vessels having very great

dimensions). In such cases, a volumeter is used to measure the volume, as shown in Fig. 22.

The volume $V_x$ to be measured is connected via cock $C$ to a vessel whose volume $V$ is known (it has been measured by the method described above). Next both vessels with cock $C$ open are evacuated with the aid of pump $P$. After this, cock $C$ is closed, and air is admitted into vessel $V$ up to a certain pressure $p_1$ measured by pressure gauge $G$. If we now open the cock again, the pressures in both vessels will become equal and a new lower pressure $p_2$ will set in, also measured by the pressure gauge. We can write the equation

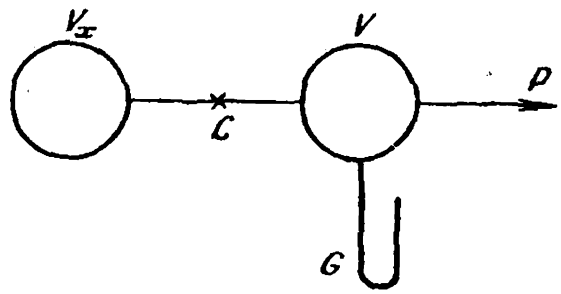



Fig. 22

of Boyle's law for the gas before and after the pressures in the two vessels become equal:

$$p_1 V = p_2(V + V_x)$$

Hence, for the required volume $V_x$ we get the formula

$$V_x = \frac{(p_1 - p_2)V}{p_2}$$

**Measuring Pressure.** The ways of measuring pressure are distinguished by their great variety both with respect to the principle of operation of the instruments and to their design.

Instruments for measuring pressure are called *manometers* or *pressure gauges*, but those intended for measuring very low pressures are frequently called *vacuum gauges*. Instruments designed specially for measuring atmospheric pressure are called *barometers*.

The pressure gauges used in practice to measure pressures include instruments which measure the pressure directly, and can therefore be called *absolute* or *primary instruments*. Other pressure gauges measure directly not the pressure, but some other quantity related to the pressure in some way or other. Such secondary instruments need preliminary graduation or, as we sometimes say, calibration. Graduation is performed by comparing their readings with those of primary instruments.

The range of pressures that have to be measured in physical investigations is exceedingly broad. The lowest pressures obtained in modern physical laboratories equal $10^{-12}$ mm Hg, and the highest ones — about $4 \times 10^5$ atm. Hence, the ratio of the highest pressure to the lowest one is about $10^{20}$.

There are naturally no instruments suitable for measuring the pressure throughout this enormous range. We have to distinguish instruments for measuring very low pressures (vacuum gauges) from pressure gauges capable of measuring high and superhigh pressures, and also from instruments measuring pressures close to atmospheric.

It is difficult to draw a sharp boundary between separate regions. We shall therefore conventionally consider pressures below 1 torr (1 mm Hg) to be low, pressures exceeding hundreds of atmospheres to be high, and pressures over 10 000 atm to be superhigh.

We shall not consider instruments for measuring low pressures in this chapter, because they will be treated in Chap. 4 specially devoted to physical phenomena in rarefied gases.

Most frequently, liquid manometers, usually filled with mercury, are employed to measure pressures ranging from 1 torr to 1 atm. A liquid manometer is a U-tube partly filled with mercury or another liquid. One limb of the tube is evacuated to a high vacuum and is soldered, or the air above the mercury in this limb is removed when the mercury is filled in so that a "Torricellian vacuum" is formed above it (Fig. 23). The second, open limb is connected to the volume being studied. The difference $h$ between the levels in both limbs indicates directly the pressure in torrs (millimetres of mercury). For greater accuracy of readings, the tubes forming both limbs must be of the same diameter. This eliminates the need to introduce special corrections connected with the meniscus of the liquid. When filling a manometer with mercury, one should take special caution to see that no gas bubbles, which are usually contained in mercury, get into the evacuated limb.

U-type liquid manometers are also employed for measuring small pressure differences. Such instruments are called *differential pressure gauges*. Figure 24 shows how such a pressure gauge is connected. It measures the difference between the pressures in vessels $A$ and $B$. If a differential pressure gauge is filled with a light liquid instead of mercury, it can be used to measure very small pressure differences up to hundredths of a torr.

If a U-tube is made of a metal instead of glass, such differential pressure gauges can be used for measuring considerable pressures, of the order of magnitude of hundreds of atmospheres. The level of the mercury can be observed in this case with the aid of a magnetic float placed on the surface of the mercury inside the tube and a magnetic pointer outside of it. When the pressure is read in this way, the material of the tube must be non-magnetic (special non-magnetic grades of steel).

Instruments designed for measuring the atmospheric pressure are called barometers, as previously indicated. The mercury manometer shown in Fig. 23, in particular, is a barometer if its second (unevacuated) limb is left open. Sometimes a barometer is given the shape shown in Fig. 25. Here both limbs, which are made from a tube having one diameter, are on

the same vertical line and are connected by a bent tube. This makes possible more accurate reading of the difference between the levels.

Liquid manometers directly measuring the pressure belong to the most accurate instruments designed for this purpose.

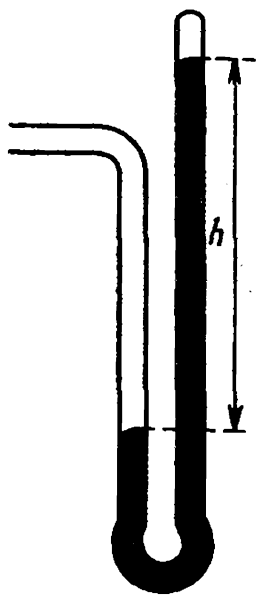



Fig. 23

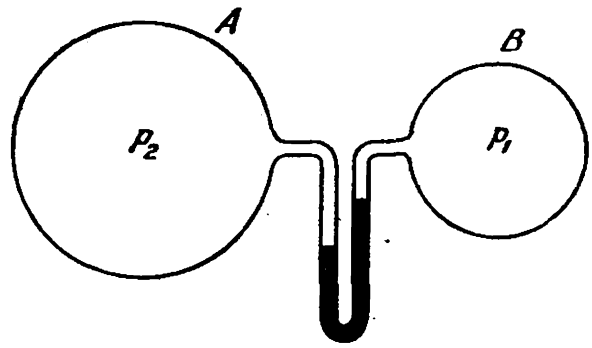



Fig. 24

Fig. 25

The Bourdon pressure gauge is used most frequently for measuring high pressures. It is shown schematically in Fig. 26. The volume being investigated is connected to the pressure gauge by means of nipple *A*. The main part of the gauge — hollow metal tube *B* having an oval cross section — is connected to the other side of the nipple. Under the action of pressure, the tube tends to straighten out so that its soldered end moves somewhat. This displacement, as shown by practical experience, is related in a simple way to the value of the pressure. An indicating mechanism with a pointer sliding along a round dial is attached to the soldered end of the tube, which is simultaneously a spring. The dial is graduated directly in units of pressure. Such pressure gauges can be used to measure pressures up to about 10 000 atm.

The Bourdon pressure gauges can also be manufactured for measuring low pressures, but such instruments are rarely used in physical investigations.

*Piston pressure gauges*, which similar to their mercury counterparts directly measure the pressure, are another important kind of pressure gauges. They are used for the graduation of secondary pressure gauges (in particular Bourdon gauges), and also for measuring high pressures. Figure 27 shows a piston pressure gauge manufactured in the USSR (type МГ-1) and intended for graduating other pressure gauges. It consists of

screw press $S$ from which the pressure is transmitted via piston $P$, and four vertical cylinders provided with valves (cocks). The pressure gauges to be graduated are connected to two of these cylinders, *1* and *2*. A piston to which plate $P_1$ carrying weights in the form of disks is screwed moves in cylinder *3*. The weights on this plate balance the pressure of the press. Cylinder *4* is intended for filling the gauge with a liquid. If $G$ is the weight

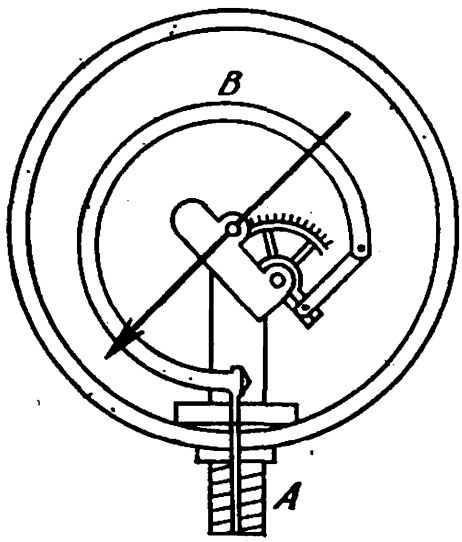



Fig. 26

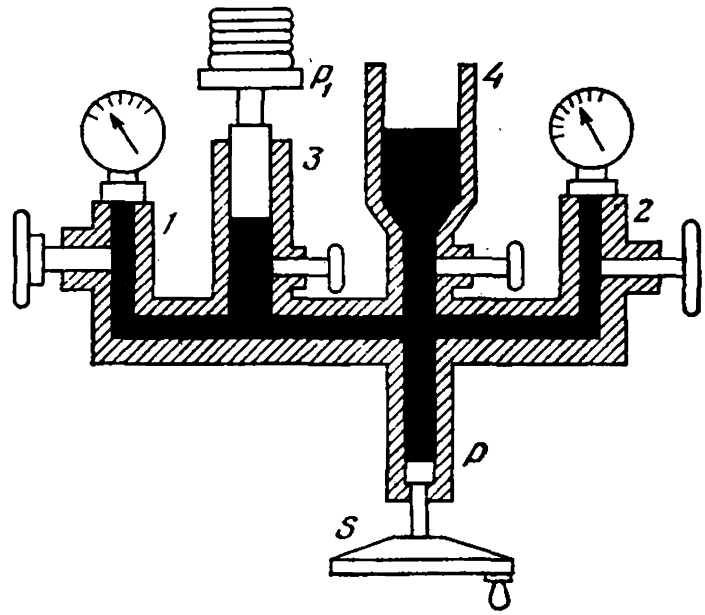



Fig. 27

of the piston with the plate and balancing weights, then the pressure $p$ is calculated by the formula

$$p = \frac{G}{A}$$

where $A$ is the area of the piston, which is understood to equal the cross-sectional area of the piston itself plus half the area of the annular gap between the piston and the cylinder in which it moves. Usually the area $A$ of the piston is close to 1 cm$^2$.

Such piston pressure gauges play the part of standard ones and are used for checking and calibrating all other instruments employed for pressure measurement. Sometimes standard Bourdon gauges are also used for this purpose, but they themselves are first calibrated according to a piston gauge.

**Measuring Temperature.** It was indicated in Sec. 1.3 that the gas thermometer, more precisely the *constant-volume gas thermometer*, has been adopted as the basis of modern thermometry. All other thermometers are graduated by comparing their readings with those of a gas thermometer.

**Gas Thermometer.** Figure 28 is a schematic view of one design of a gas thermometer. It consists of vessel $A$ containing a gas and mercury manometer $M$. Thin capillary tube $C$ joins the manometer to the vessel. A branch, also a capillary tube, leads from capillary $C$ to a device intended for filling vessel $A$ with the gas. This device consists of open vessel $V$ with mercury connected by means of a flexible hose to a tube provided with cock $c_1$ from which a branch with cock $c_2$ leads off. It is exactly through this branch that the gas is admitted with cocks $c_1$ and $c_2$ open and with vessel $V$ lowered. After the required amount of gas has been admitted, cock $c_2$ is closed and vessel $V$ is lifted so that the mercury rises almost to the lower end of the capillary branch, and then cock $c_1$ is also closed. Vessel $A$ with capillary $C$ is thus separated from the external space by a mercury seal.

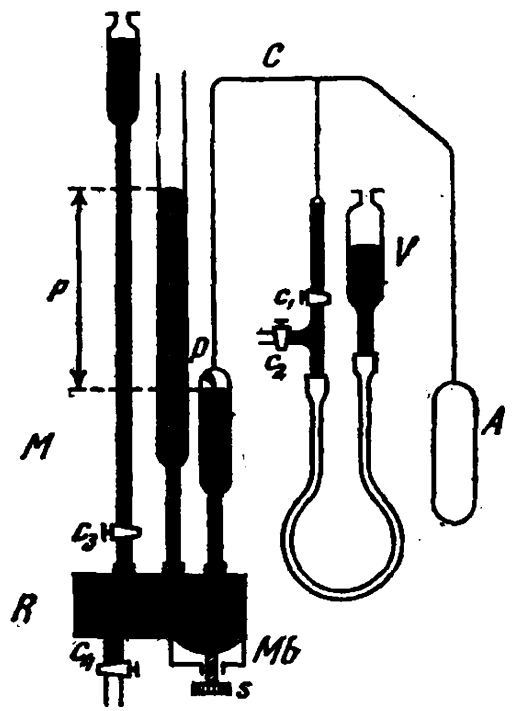



Fig. 28

A constant volume is ensured by keeping the mercury in the right-hand limb of the pressure gauge at the level of the end of point $P$. The level is adjusted by supplying mercury from spare reservoir $R$ via cock $c_3$ or draining it from the reservoir via cock $c_4$. Exact adjustment of the level is performed with the aid of screw $s$ which acts on flexible steel membrane $Mb$.

Since only the gas in vessel $A$ is the thermometric substance in the thermometer, while the gas filling the volume of the capillary tube and the part of the volume of the right-hand limb of the manometer up to the point "participates" in creating the pressure, then this part of the volume of the gas is a "harmful" volume that introduces an error into the measurements. It must therefore be as small as possible in comparison with the volume of vessel $A$.

In measuring temperature, vessel $A$ is brought into contact with the body whose temperature is to be measured, and after thermal equilibrium sets in the pressure $p$ is read off the manometer (see Fig. 28). The temperature is calculated by the formula

$$T = \frac{p}{p_0} \times 273.15$$

Here $p_0$ = pressure of the gas at a temperature of 0 °C (273.15 K), which must be determined in a special experiment

$p$ = pressure read off the manometer and corrected with account taken of various errors connected with the existence of the "harmful" volume, with thermal expansion of the vessel, etc.

Gas thermometers use either helium (in measuring low temperatures) or nitrogen (for high temperatures at which helium penetrates through the walls of the vessel).

Gas thermometers are used to measure temperature within a broad interval, approximately from 4 K to the melting point of gold (1337.58 K or 1064.43 °C).

Gas thermometers are not used for technical measurements in practice, however. They are important in that they are the *primary* instruments for measuring temperature according to which *secondary* thermometers are graduated whose action is based on the use of other thermometric substances and quantities. Secondary thermometers are graduated either directly according to a gas thermometer (which is done quite rarely) or by using the so-called *International practical temperature scale.* The latter is based on a number of *defining fixed points* (datum points), i.e. temperatures which definite numerical values measured with the aid of a gas thermometer are assigned to. The International temperature scale, adopted in 1968, is based on the defining fixed points given in Table 3.

*Table 3*

| Defining fixed points of International temperature scale | Assigned temperature values | |
|---|---|---|
| | K | °C |
| Triple point of hydrogen | 13.81 | −259.34 |
| Boiling point of hydrogen | 20.28 | −252.87 |
| Boiling point of neon | 27.102 | −246.048 |
| Boiling point of oxygen | 90.188 | −182.962 |
| Triple point of water | 273.16 | 0.01 |
| Boiling point of water | 373.15 | 100 |
| Freezing point of zinc | 692.73 | 419.58 |
| Freezing point of silver | 1235.08 | 961.93 |
| Freezing point of gold | 1337.58 | 1064.43 |

Secondary thermometers in the greatest favour include liquid-filled (liquid-expansion) thermometers, resistance thermometers, and thermocouples.

**Liquid-Filled Thermometers.** Liquid-filled thermometers have been in use for a long time in engineering and everyday life, but are not accurate enough for use in physical investigations. The region of their application is limited from the side of low temperatures by the properties of the liquid used in them, and from the side of high temperatures by the properties of

the glass. At low temperatures, the liquids freeze, and at high ones, the glass softens. Nevertheless, liquid-filled thermometers can be used within a quite broad range of temperatures, from −200 to +600 °C.

The following liquids are mainly used in these thermometers:

pentane, for temperatures from −200 to +20 °C;
ethyl alcohol, from −110 to +50 °C;
toluene, from −70 to +100 °C;
mercury, from −38.87 to +600 °C.

The design of mercury thermometers is generally known, and for this reason we shall not describe it in detail. We shall only indicate that there are two main kinds of these thermometers. The first consists of a reservoir with mercury of a cylindrical or spherical shape (the former is preferred) to which a thin and thin-walled capillary tube of glass of the same grade is soldered. Behind the capillary tube there is installed a scale of metal or milk glass on which degrees (kelvins) and fractions of a degree are marked in graduation. These thermometers cannot be used for measuring high temperatures because above 356 °C (the boiling point of mercury at atmospheric pressure) the capillary tube must be specially filled with a gas under a high pressure. A thin-walled capillary tube, however, cannot withstand the required pressure of the gas, which reaches 20 and even 70 atm. For this purpose, thermometers with thick-walled capillary tubes, the so-called stem thermometers, are suitable. The outer diameter of the capillary tube in them is almost the same as that of the reservoir, and the scale is marked by etching on the capillary tube itself.

In accurate measurements, numerous corrections, for which the corresponding formulas exist, must be introduced into the readings of a mercury thermometer.

The other liquids used for liquid-filled thermometers differ from mercury first of all in that they wet glass. Therefore, to prevent the appearance of a gap in the column of liquid, the capillary tubes of the thermometers must always be filled with a gas, and not only at high temperatures. An important feature of these thermometers is also the non-uniformity of their scales, i.e. different sizes of the degree or kelvin graduations at different parts of the scale. This is the result of the features of thermal expansion of the liquids.

**Resistance Thermometers.** The thermometric body in these thermometers is usually a metal wire, and the thermometric quantity is the electric resistance of the wire. Like liquid-filled thermometers, they require graduation according to a gas thermometer or some other thermometer whose readings have already been related to those of a gas thermometer.

The resistance of a metal with increasing temperature grows according to a quite definite law, which by itself also depends on the temperature, so that in different temperature regions we have to use different formulas for the temperature dependence of the resistance.

Pure platinum and copper are the most favoured metals for resistance thermometers. Platinum is suitable for measuring the temperature within a broad range of values from −200 to +1100 °C, copper — for the smaller interval from −20 to +100 °C. A platinum thermometer made of very pure metal has been recommended by the International Committee of Weights and Measures for reproducing the thermodynamic scale of temperatures within the region from −190 to +660 °C.

Upon a change in temperature by one kelvin, the resistivity of platinum (and of many other metals) near room temperature changes by 0.4%, which is very close to 1/273 — the temperature coefficient of the change in volume and pressure of ideal gases. This quantity is called the *temperature resistance coefficient*. The above value of the temperature coefficient allows us to measure a temperature change of several thousandths of a kelvin because the measurement of the temperature consists in measuring the resistance, which can be done with a high accuracy attended by a very great sensitivity.

Resistance thermometers are also employed for measuring very low temperatures, but in this case they are made of other substances instead of platinum and copper, mainly of bronze and carbon (graphite).

A special kind of resistance thermometers are *thermistors*. Here the thermometric body is not a metal, but a semiconductor which differs from a metal in that its resistance diminishes instead of growing with increasing temperature. In addition, the temperature resistance coefficient of semiconductors is about 10 times greater than that of metals while the resistivity is tens and hundreds of times greater. These two features impart an exceedingly great sensitivity to semiconductor resistance thermometers, and they can be very tiny in size. The dimensions of thermistors do not generally exceed a few millimetres, and they can be reliably used to measure changes in temperature of thousandths of a kelvin.

The semiconductor thermistors produced in the Soviet Union are intended for measuring temperatures ranging from −100 to +120 °C. The temperature-sensitive element of these instruments has the form of a rod, plate, or bead.

The low-temperature carbon resistance thermometers mentioned above can also be related to semiconductor thermometers because their temperature resistance coefficient has the same sign as that of semiconductors — the resistance diminishes with increasing temperature (true, for other reasons).

**Thermocouples.** These are an important kind of secondary thermometers. Here a phenomenon known as the Seebeck effect is used. Its essence is that if a circuit is formed of two different conductors $A$ and $B$ (Fig. 29) soldered at their ends, an electromotive force will appear in the circuit provided that the junctions are at different temperatures. The magnitude of this so-called thermoelectromotive force (thermo-e.m.f.) depends on the difference between the temperatures of the junctions. If one junction is kept at a constant temperature $T_1$, then the thermo-e.m.f. will depend

only on the temperature $T_2$ of the other junction. Hence, the device shown in Fig. 29 and called a thermocouple can be used for measuring temperature.

Thus, the thermocouple itself is the thermometric body in a thermocouple thermometer, and its thermo-e.m.f. is the thermometric quantity.

An instrument measuring the e.m.f. (a millivoltmeter) is included in the circuit of a thermocouple to measure its thermo-e.m.f. It can be connected in either of the two ways shown in Fig. 30. In the first case, one junction remains free, and it is brought into contact with the body whose temperature is to be measured. In the second case, both junctions are free. One of them must be kept at a strictly constant temperature (it is usually placed in a vessel containing melting ice). The other junction is brought into contact with the body being investigated. The second scheme is preferable for accurate measurements because the readings of the instrument do not depend on the ambient temperature.

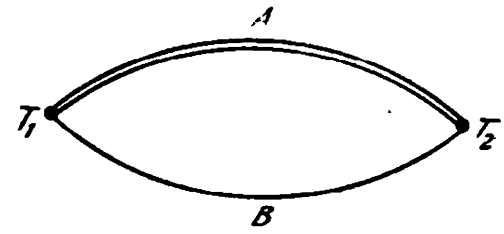


Fig. 29

The thermocouples used for measuring temperature must have the highest possible numerical value of the thermo-e.m.f., a great dependence of the latter on the temperature, the simplest possible form of the law relating the thermo-e.m.f. to the temperature, and stability of the thermocouple materials in conditions of high temperatures.

Data on thermocouples that are most frequently used to measure temperatures are given in Table 4.

The platinum-platinum/rhodium thermocouple, distinguished by its high stability at elevated temperatures, is of special significance. The International Committee of Weights and Measures has decided that this thermocouple is to be used for reproducing the thermodynamic temperature scale in the region from 660 to 1063 °C.

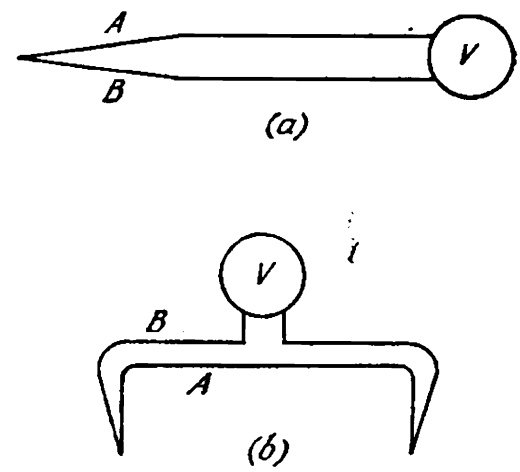


Fig. 30

Other thermocouples are used in addition to those listed above. They include Chromel-constantan, platinum/rhodium-gold/palladium, and iridium-an iridium and ruthenium alloy (this thermocouple can measure temperatures up to 2000 °C).

**High and Low Temperatures.** The measurement of very high temperatures (of thousands of kelvins and higher) encounters the obvious difficulty that there are no refractory thermometers which can be brought into

*Table 4*

| Thermocouple | Composition of alloys | Range of temperatures measured, °C |
|---|---|---|
| Platinum-platinum/rhodium | Pt —90%, Rh—10% | From 0 to +1700 |
| Iron-constantan | Cu—55%, Ni—45% | From —200 to +600 |
| Chromel-Alumel | Ni —90%, Cr—10%; Ni —95%, Al—2%, Mn—2%, Si—1% | From —200 to +1350 |
| Chromel-Copel | Ni —43%, Cu—57% | From —50 to +800 |
| Copper-constantan | | From —200 to +600 |

contact with such greatly heated objects. Hence, in this region of temperatures, the heated body itself becomes the thermometric body while the energy it emits in the form of light becomes the thermometric quantity. Measurement of this energy does not require direct contact with its source.

The physical laws used here and the instruments *(pyrometers)* with whose aid the emitted energy is measured will be described in the course of optics. Here we shall only note that according to a decision of the International Committee of Weights and Measures, the thermodynamic temperature scale above 1063 °C is reproduced with the aid of a pyrometer.

Great difficulties are also encountered when measuring very low temperatures (below 1 K). First of all, experience shows that at these temperatures simple contact of a thermometer with the cooled body does not result in their temperatures becoming equal for a long time. Besides this, many thermometric quantities that are suitable for use at higher temperatures "fail" in the region of temperatures being considered. For example, the pressure of gases becomes immeasurably low, and the resistance stops depending on the temperature. Therefore here also, as with extremely high temperatures, the cooled body itself becomes the thermometric body. It will be shown in Chap. 8 that the lowest temperatures are obtained with the aid of paramagnetic salts. This allows us to use the paramagnetic susceptibility of these salts, which is the main characteristic of their magnetic properties, as the thermometric quantity. Serious and still unsurmounted difficulties appear here, however. They are connected with coordination of the temperature measured in this way with the thermodynamic temperature scale. Space does not permit us to consider the details of this problem in the present course.

CHAPTER 2

# KINETIC THEORY OF HEAT. LAW OF CONSERVATION OF ENERGY

In this chapter, we shall turn to the energy aspect of the process of a change in the state of an ideal gas and shall first consider how a change in the temperature of a gas affects its state.

## 2.1. INTERNAL ENERGY OF AN IDEAL GAS

The mean energy of a molecule of an ideal gas, if its molecules are considered as points, is determined by the expression

$$\frac{m\overline{v^2}}{2} = \frac{3}{2}kT$$

It must be noted once more that this expression holds for point molecules that are capable of performing only translational motion. Such a notion of a gas may be considered true for monatomic gases. If a molecule of a gas contains more than one atom, however, it may perform other kinds of motion — rotational and vibrational, also involving a certain energy.

We shall meanwhile limit ourselves to monatomic gases and write an expression for the energy of all the molecules of a given mass of a gas. If the gas contains $N$ molecules, their total energy $U$ is

$$U = \frac{3}{2}NkT \tag{2.1}$$

For one mole, this expression becomes

$$U = \frac{3}{2}N_0kT = \frac{3}{2}RT \tag{2.2}$$

This energy is called the *internal energy* of an ideal gas.

In general by the internal energy of a body is meant the total energy relating to the molecules themselves, i.e. their "invisible" energy. The latter includes the kinetic energy of motion of the molecules themselves, the kinetic energy of motion of the atoms inside a molecule (if the molecule is not monatomic), the potential energy of interaction between the atoms in the molecule, and even the kinetic energy of the particles which the atoms consist of (the nuclei and electrons). It does not include, however, the kinetic energy which the gas may have if it is in motion as a whole, and the potential energy which it may have if it is in the field of forces.

The internal energy of a given mass of an ideal gas, as follows from Eqs. (2.1) and (2.2), depends only on the temperature and does not depend on the pressure or the volume of the gas. (This is not true for real gases.)

Examination of Eqs. (2.1) and (2.2) shows that to change the temperature of a gas its internal energy must be changed. A change in energy, as is known from mechanics, is connected with work. The energy of a body changes if the body performs work or work is performed on the body, and this change exactly equals the work done.

Hence, it would seem to follow that the temperature of a gas or in general of any body can be changed only at the expense of mechanical work: work must be done on a body to heat it, and conditions must be created in which the body itself could perform work to cool it. Experience shows that the temperature of a body can really be changed by spending the corresponding amount of mechanical work. For example, when two bodies are rubbed against each other, they get heated (the ancient way of getting fire is based on such friction). It will be shown below that a gas can also be heated as a result of work being done.

## 2.2. QUANTITY OF HEAT

We know, however, that a gas, like any other body, can also be heated or cooled in a different way, in which work seems to play no part. It consists in bringing a body into contact with another body having a different temperature. The same result can also be achieved without direct contact when two bodies having different temperatures are separated by a medium or even by a vacuum. In the first case, heating or cooling is said to be accomplished by thermal conduction, in the second by radiation.

But it follows from Eq. (2.1) that a change in the temperature of a gas is always related with a change in energy. When this change occurs as a result of work being done, the cause of the change is obvious because work is a change in energy. Hence in the "contact" method too, energy is supplied (in heating) or removed (in cooling) in some way or other.

The mechanism of transferring energy in the "contact" method consists in that the particles of the contacting bodies exchange energy when they collide with one another. The particles of the hotter body lose their energy, transferring it to particles of the colder partner. Hence, in this case instead

of a change in energy because of work being done, the same result is achieved by the transfer of the energy of chaotically moving particles of one body to particles of another body.

Owing to circumstances connected with the history of development of physics, however, when the change in the temperature (heating or cooling) of a body occurs by the contact method or by radiation, a certain *quantity of heat* is said to be supplied to the body or removed from it.

Consequently, the quantity of heat is the *energy* transferred from one body to another upon their contact (directly or via a third body) or by radiation. In essence, when heat is transferred, we also have to do with work. The latter is done in this case, however, not by macroscopic orderly moving bodies, but by chaotically moving microparticles. We shall see below that this circumstance is very important.

## 2.3. THE MECHANICAL EQUIVALENT OF HEAT

There is no other difference between heat and work (energy). They must therefore be measured in the same units. In the SI system, the unit of the quantity of heat is the joule (J). But owing to historical reasons, the quantity of heat up to recent times was measured in calories and kilocalories. A special unit for the quantity of heat was introduced back in the "prekinetic" times when heat was considered to be a special substance capable, like a fluid, to flow from one body to another. At present, when the equivalence of energy and heat is clear, this unit has lost its physical meaning, but according to tradition has been retained in both physics and engineering.

The kilocalorie is defined as the quantity of heat whose supply (or removal) causes one kilogram of water at atmospheric pressure to become heated (or cooled, respectively) by one kelvin.

The equivalence of heat and energy was especially clearly demonstrated back in the fifties of last century by J. Joule. He showed by a series of painstaking experiments that the heating caused by one kilocalorie of heat is the same as is produced by a quite definite and always identical amount of work. Namely, it was found that

$$1 \text{ kcal} = 4186.8 \text{ J}$$

Similarly for the gramme-calorie, or simply calorie (cal), which is one-thousandth of a kilocalorie, we have

$$1 \text{ cal} = 4.1868 \text{ J}$$

The number showing the ratio between a unit of mechanical work and a unit of heat is called the *mechanical equivalent of heat:*

$$E = 4186.8 \text{ J/kcal} = 4.1868 \text{ J/cal}$$

The reciprocal of this quantity is called the *thermal equivalent of mechanical work:*

$$E' = 2.39 \times 10^{-4} \text{ kcal/J} = 0.239 \text{ cal/J}$$

We shall not use these equivalents in the following sections. When an equation includes both the quantity of heat and work or energy, we shall consider that they are measured in the same units (in calories or in joules, it makes no difference).

## 2.4. THE FIRST LAW OF THERMODYNAMICS

A change in the state of a body or system of bodies, generally speaking, is attended by work performed by this system, or by work performed on it by external forces. This work can be expressed through the parameters determining the state of the system.

If, as we already know, the state of a body is determined by two of the three parameters $p$, $V$, and $T$, then in the general case a change in any of them must be attended by external work.

For instance, a change in the temperature of a gas, i.e. its heating or cooling, may be accomplished as a result of the expenditure of mechanical work from outside (heating) or at the expense of work done against external forces (cooling).

This mechanical work is performed when a gas is compressed by an external force and gets heated, or upon the expansion of a gas when it itself performs work and cools during the process. The volume of a gas can be changed without changing its temperature (see below), and less work is correspondingly needed in this case.

But, as already indicated, the state of a gas (or other bodies) can be changed by imparting to it or, conversely, by removing from it a *certain quantity of heat*, i.e. by bringing it into contact with a hotter or a colder body.

What work will be done in this method of changing the state? The answer to this question is given by the *law of conservation of energy*. If a certain quantity of heat $dQ$ is supplied to a gas (or some other body), the work $dW$ will be performed, generally speaking, and its *internal energy* will change by $dU$.

The law of conservation of energy states that *the work done by a system equals the difference between the quantity of heat supplied to the system and the change in its internal energy*:

$$dW = dQ - dU$$

or

$$dQ = dU + dW \tag{2.3}$$

This equation expresses a very important law of nature, the law of conservation of energy as applied to mechanical and heat energy. This law has been named the *first law of thermodynamics*.

**Work in Changing the Volume of a Gas.** It is not difficult to calculate the work connected with the expansion or compression of a gas, i.e. with

a change in its volume. Suppose the gas is in a cylinder closed with a movable piston whose area is $A$ (Fig. 31). Suppose further that when an external force $F$ is applied, the piston lowers over the distance $dx$, compressing the gas. The latter will be compressed until the force $F$ is balanced by the force acting on the piston from the side of the gas and equal to $pA$, where $p$ is the pressure of the gas. The work $dW$ done to move the piston over the distance $dx$ is obviously equal to $pA\,dx$. But $A\,dx$ is nothing but the change in the volume of the gas $dV$ in compression, i.e.

$$A\,dx = -dV$$

whence

$$dW = -p\,dV \qquad (2.4)$$

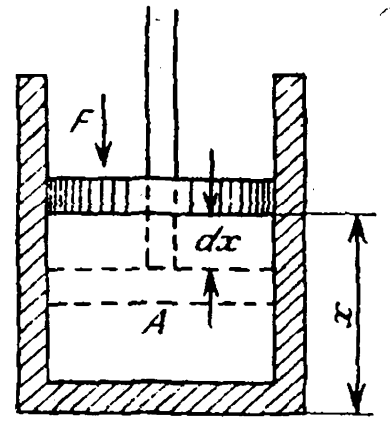


Fig. 31

Conversely, when the gas expands, i.e. when its volume grows by $dV$, the gas itself does work against the external forces equal to $+p\,dV$.

*A change in the volume of a gas is attended by work equal to the product of the pressure of the gas and the change in its volume.*

Equation (2.4) holds not only for a gas, but also for any bodies. If upon a change in the state of a body external work is done only at the expense of a change in volume, the first law of thermodynamics can be written in the form

$$dQ = dU + p\,dV \qquad (2.5)$$

Cases are possible when the change in the state of bodies is attended by a change in electrical, magnetic or other parameters. The corresponding addends — the electrical, magnetic, and other kinds of energy — should therefore be included in the right-hand side of Eq. (2.5). Here we shall consider only changes in the parameters $p$ and $V$.

We can also calculate the external work when the change in the parameters of state is not infinitely small.

If a body passes from state *1* to state *2*, the work $W$ connected with this transition is determined by integration of Eq. (2.4):

$$W = \int_1^2 dW = \int_1^2 p\,dV$$

This integral can be determined graphically. Indeed, the state of a body, as indicated above, is characterized by a point on the curve $p = f(V)$. Hence, if the relationship $p = f(V)$ has been constructed graphically, for

example if it is expressed by curve *I* in Fig. 32, then the integral $\int_1^2 p\,dV$ equals the hatched area under this curve.

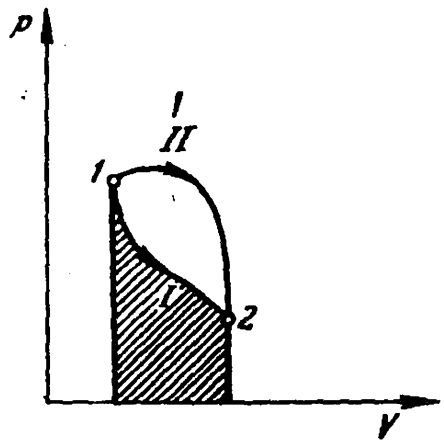



Fig. 32

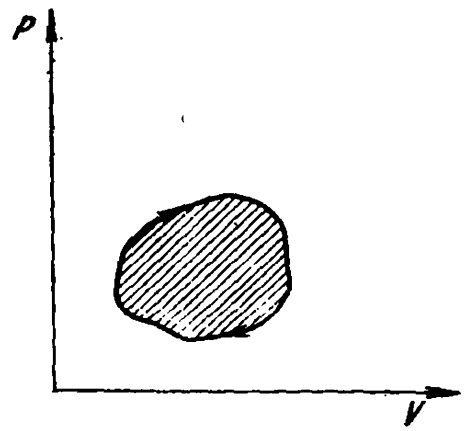



Fig. 33

If the transition from state *1* to state *2* occurs so that the change in pressure with volume is shown by curve *II*, then the work involved in this transition will be different.

*The external work done by a body (or on it) upon a change in its volume depends on the sequence of the states which the body passes through from its initial to its final state.*

As regards the *internal* energy $U$, it depends *only* on the state of the body, and its change does not depend on the intermediate states which the body was in.

Consequently, Eq. (2.5) can be rewritten in the form

$$\int_1^2 dQ = U_1 - U_2 + \int_1^2 p\,dV$$

where $U_1$ and $U_2$ are the values of the internal energy of the body in states *1* and *2*, respectively.

In a special case if a body as a result of all the changes in its state has returned to its initial state, i.e. $U_1 = U_2$, the process of the change in state is said to be *cyclic*. Such a process is depicted graphically by a closed curve (Fig. 33), and the work done (or spent) is determined by the hatched area.

If the work

$$W = \int p\,dV$$

during a cycle is positive, i.e. the body itself has done work against external forces, this means that it has *received* an equal quantity of heat $Q$ from its

*surroundings*. If this work $W$ during a cycle is negative, i.e. external forces have performed work on the body, a quantity of heat $Q$ equal to it has been *liberated*.

Thus, in a cyclic process

$$Q = W$$

Our reader should not be confused by the unusual form of the curve $p = f(V)$ in Figs. 32 and 33 when on some of its portions the pressure grows with an increase in the volume. The "usual" relationship, when the pressure is inversely proportional to the volume of a gas, is observed only at constant temperature, i.e. in an isothermal process. The process of the change in the volume of a gas which we are considering, however, relates to the case when a certain quantity of heat is imparted to the gas or removed from it, and work is done on it (or it itself does work), and at different stages of the change in volume the temperature of the gas is different.

There is nothing surprising in the fact that together with expansion (lifting of the piston) a gas can increase its temperature to such an extent at the expense of a heat source that its pressure will grow notwithstanding the increase in the volume (and, conversely, upon compression a gas can give up heat to a colder body and its pressure will lower).

This also explains the circumstance that when passing from the same initial state ($p_1$, $V_1$) to the same final state ($p_2$, $V_2$) through different intermediate states a different quantity of work is obtained, and, therefore, in a cyclic process it does not equal zero. The work of all heat engines is based on exactly this principle.

It is hardly necessary to stress that no positive work can be done by a body if its temperature is constant during an entire cyclic process (i.e. if the process is isothermal). In a gas, such an isothermal *cyclic* process is in general impossible because if the pressure changes with the volume along an isotherm, then it is possible to return to the initial state only along the same isotherm. Such a process, however, cannot be called cyclic in the sense mentioned above.

**Quasistatic Processes.** In deriving Eq. (2.4) for the work of a gas connected with a change in its volume, it was taciturnly assumed that during the *entire* process of the change in volume the pressure at each moment of time is identical at all points of the gas. Otherwise, the value of the pressure $p$ would be absolutely indefinite. It is not so simple as it seems, however, to ensure such a constancy of the pressure throughout the entire volume of a gas (or of any body, as a matter of fact).

If a gas expands or is compressed *rapidly*, then the pressures in different parts of it do not have time to become equalized. The difference of the pressures causes the gas to flow with different velocities at different points and, particularly, causes eddy currents. These movements require a certain

amount of work for their creation. In addition, different parts of a gas may have different temperatures and densities.

In short, a gas is not in a *state of equilibrium* when its volume changes rapidly. For a gas to be in equilibrium in the process of a change in its volume (or some other quantity characterizing its state), this process must occur very slowly, in the limit — infinitely slowly. In this case, all the deviations from equilibrium will have time to vanish, the gas will pass through a *number of states of equilibrium*, one turning into another.

Such processes are called *quasistatic* because at each given moment the state of a gas differs only slightly from a static state when the parameters of state are identical throughout the entire volume. It is clear that only quasistatic processes can be graphically represented in the form of curves like those, for example, in Fig. 32 or Fig. 4 (p. 34). It is impossible to depict a non-quasistatic process. Equation (2.4) and its corollaries can be used only for quasistatic processes. (For greater details see Chap. 6.)

If a process of a change in volume, i.e. compression or expansion of a gas, proceeds non-quasistatically, the work done in compression or expansion will be less than in a quasistatic process. This can be understood from the following considerations. Assume that a gas in a vessel with a piston (see Fig. 31) is first in equilibrium. This means that the pressure $p$ of the gas inside the vessel equals the external pressure. Suppose that something made the gas expand (non-quasistatically), i.e. the piston began to move upward. Hence, the external pressure $p_1$ became less than the equilibrium pressure $p$, and, therefore, the external work

$$p_1 \, dV < p \, dV$$

Correspondingly, in non-quasistatic compression of a gas, its external pressure $p_1$ is greater than the equilibrium value, and, therefore, the work (this time it is negative)

$$-p_1 \, dV < -p \, dV$$

And only in a quasistatic process does the external pressure infinitely slightly differ from the equilibrium value, and, therefore, the work done in this case is maximum.

Moreover, a gas may expand without performing any external work at all. This can be done by connecting to each other two vessels, of which one is filled with a gas and the other is empty. The gas will flow from the first vessel to the second and will therefore occupy a greater volume. But no work (external) will be performed (because there are no external forces against which this work could be done). This is the so-called process of expansion into a vacuum (see Sec. 2.14). And indeed, during this entire process the gas is not in equilibrium (no matter how slowly the process goes on).

## 2.5. HEAT CAPACITY OF IDEAL GASES

Let us now determine the quantity of heat that must be imparted to an ideal gas for its heating or removed from it for its cooling.

It is clear from the preceding section that the quantity of heat needed for changing the temperature of a gas depends on whether work is performed at the same time, i.e. whether the volume of the gas changes.

If a gas being heated (or cooled) is confined in a vessel enclosed from all sides whose volume cannot change (we shall disregard here the thermal expansion of the material of the vessel), the heat $dQ$ supplied to it is used exclusively for changing its internal energy. The pressure of the gas in heating will grow according to a law which we already know. If the gas is in a vessel similar to that shown in Fig. 31, it will expand, performing the work of lifting the piston and retaining its pressure constant. The heat supplied in this case is determined by Eq. (2.5):

$$dQ = dU + p\,dV$$

It is clear that a greater quantity of heat is needed when the pressure of the gas is kept constant.

The quantity of heat needed for heating a gas depends on the amount of gas heated and by how many kelvins its temperature is to be changed. The greater these two factors are, the greater is the quantity of heat needed. Therefore, a special quantity — *heat capacity* — is used to characterize the thermal properties of a gas.

*The heat capacity of a body is the quantity of heat that must be supplied to it or removed from it to change its temperature by one kelvin.*

The heat capacity related to a unit mass of a substance is called the *specific heat capacity*. It characterizes the substance which a body consists of instead of the body itself.

The heat capacity related to one mole of a substance is called the *molar heat capacity*. Like the specific heat capacity, it characterizes the substance.

It is obvious from the definition of heat capacity that the heat capacity of a body is expressed in J/K. Accordingly, the specific heat capacity is measured in J/kg·K, and the molar heat capacity in J/mol·K.

If the quantity of heat is measured in calories, then the specific heat capacity is measured in cal/g·K, and the molar heat capacity in cal/mol·K. It is clear that

$$1\ \text{cal/g·K} = 4186.8\ \text{J/kg·K} \quad \text{and} \quad 1\ \text{cal/mol·K} = 4.1868\ \text{J/mol·K}$$

The following expression relates the specific heat capacity $c$ to the molar heat capacity $C$:

$$c = \frac{C}{\mu}$$

where $\mu$ is the molar mass of a substance (numerically equal to the mass of a mole).

If a mole of a substance is heated not by one kelvin, but by $dT$ kelvins, the quantity of heat spent for this is

$$dQ = C\,dT$$

whence

$$C = \frac{dQ}{dT} \tag{2.6}$$

Assume that heating occurs in conditions when the volume remains constant ($V = \text{const}$). The corresponding molar heat capacity is called the *molar heat capacity at constant volume*, or the *isochoric molar heat capacity*, and is designated by $C_V$:

$$C_V = \left(\frac{dQ}{dT}\right)_V \tag{2.7}$$

Since here heat is spent only for changing the internal energy $dU$, then $dQ = dU$ and

$$C_V = \left(\frac{dU}{dT}\right)_V \tag{2.8}$$

Hence, $dU = C_V\,dT$. The equation of the law of conservation of energy (2.5) can now be rewritten in the form

$$dQ = C_V\,dT + p\,dV \tag{2.9}$$

Consequently, the heat supplied to a body is used for changing the temperature $dT$ (a change in the internal energy) and for changing the volume $dV$ (external mechanical work is connected with this change).

If the pressure remains constant in heating, the heat capacity is called the *heat capacity at constant pressure* $C_p$ (it can also be called the *isobaric heat capacity*):

$$C_p = \left(\frac{dQ}{dT}\right)_p$$

Using the results of the kinetic theory of gases, we can easily calculate the molar heat capacities of an ideal gas.

## 2.6. HEAT CAPACITY OF MONATOMIC GASES

We have seen that for an ideal monatomic gas the internal energy of a mole equals $U = 3RT/2$; hence,

$$C_V = \frac{3}{2}R \tag{2.10}$$

If we divide this value of the molar heat capacity by the number of molecules in a gramme-molecule, i.e. by the Avogadro constant, we get the average contribution of each molecule to the heat capacity of a gas:

$$\frac{3}{2}\frac{R}{N_A} = \frac{3}{2}k$$

Consequently, when the temperature rises by one kelvin, the energy of each molecule grows on an average by $3k/2$ joules.

The heat capacity $C_p$ of an ideal gas at constant pressure is greater than the heat capacity $C_V$ at constant volume by the amount of work performed by a mole of the gas in expanding when heated by one kelvin. This work equals $p(\partial V/\partial T)_p$. Thus,

$$C_p = C_V + p\left(\frac{\partial V}{\partial T}\right)_p = \frac{3}{2}R + p\left(\frac{\partial V}{\partial T}\right)_p \qquad (2.11)$$

But for a mole of an ideal gas, we have $pV = RT$, therefore, $p(\partial V/\partial T)_p = R$, and

$$C_p = \frac{3}{2}R + R = \frac{5}{2}R \qquad (2.12)$$

Inspection of Eqs. (2.10) and (2.12) shows that the molar heat capacity at constant pressure exceeds that at constant volume by the quantity $R$:

$$C_p - C_V = R$$

Hence, *the molar gas constant numerically equals the work which one mole of an ideal gas performs in expanding when heated by one kelvin.*

Since $R = 8.314$ J/mol, we get the following values for the molar heat capacities $C_V$ and $C_p$:

$$C_V = \frac{3}{2}R = \frac{3}{2} \times 8.314 = 12.47 \text{ J/mol} \cdot \text{K}$$

$$C_p = \frac{5}{2}R = \frac{5}{2} \times 8.314 = 20.78 \text{ J/mol} \cdot \text{K}$$

The molar gas constant $R$ can also be expressed in the units cal/mol·K. Since 1 J = 0.239 cal, then

$$R = 1.988 \text{ cal/mol} \cdot \text{K} \approx 2 \text{ cal/mol} \cdot \text{K}$$

Hence for $C_V$ and $C_p$, we get the values

$$C_V \approx 3 \text{ cal/mol} \cdot \text{K} \quad \text{and} \quad C_p \approx 5 \text{ cal/mol} \cdot \text{K}$$

The difference between these heat capacities equals

$$C_p - C_V = R \approx 2 \text{ cal/mol} \cdot \text{K} \qquad (2.13)$$

and their ratio

$$\gamma = \frac{C_p}{C_V} = 1.66 \tag{2.14}$$

Table 5 gives experimental values of the molar heat capacities that well agree with the calculated data for monatomic gases (and as indicated above, it is exactly for these gases that our theory should be true). Indeed, from Eq. (2.10) it follows that $C_V/R = 1.5$, and from Eqs. (2.13) and (2.14) we have $(C_p - C_V)/R = 1$ and $\gamma = C_p/C_V = 1.66$.

A glance at Table 5 shows that the experimental data agree with the theoretical ones.

*Table 5*

**Heat Capacity of Monatomic Gases**

| Gas | $\frac{C_V}{R}$ | $\frac{C_p - C_V}{R}$ | $\frac{C_p}{C_V}$ | Gas | $\frac{C_V}{R}$ | $\frac{C_p - C_V}{R}$ | $\frac{C_p}{C_V}$ |
|---|---|---|---|---|---|---|---|
| Helium | 1.519 | 1.001 | 1.659 | Krypton | — | — | 1.68 |
| Neon | — | — | 1.64 | Xenon | — | — | 1.66 |
| Argon | 1.5 | 1.008 | 1.67 | | | | |

**Enthalpy.** If we supply a certain quantity of heat to a gas so that its pressure remains constant, i.e. we allow it to expand freely, we can rewrite the equation expressing the first law of thermodynamics in the form

$$(dQ)_p = d(U + pV)$$

Indeed

$$d(U + pV) = dU + p\,dV + V\,dp$$

But if the pressure remains constant, then $dp = 0$ and, accordingly,

$$d(U + pV) = dU + p\,dV$$

This means that if a gas (or any body) is heated or cooled at constant pressure, the heat supplied to or removed from it equals the change in the quantity

$$H = U + pV$$

which is called the *enthalpy*. (In engineering, this quantity is often called the *heat content*.)

The enthalpy can also serve as a parameter determining the state of a gas if the change in state occurs at constant pressure. The heat capacity of a gas at constant pressure can obviously be expressed through the enthalpy:

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \frac{dH}{dT}$$

For an *ideal* monatomic gas, the enthalpy of a given mass of a gas is proportional to the temperature and does not depend on the volume it occupies:

$$H = U + pV = \frac{3}{2} RT + RT = \frac{5}{2} RT$$

hence,

$$C_p = \frac{5}{2} R$$

For a real gas, the enthalpy depends on the volume. We can see that at constant pressure the properties of the enthalpy $H$ are similar to the properties of the internal energy $U$ at constant volume.

## 2.7. HEAT CAPACITY OF GASES AND NUMBER OF DEGREES OF FREEDOM OF MOLECULES

For comparison with the results of theoretical calculations of heat capacity, we have chosen experimental data relating to monatomic gases, i.e. gases whose molecules consist of a single atom (see Table 5). And this has not been done by chance. One of the assumptions underlying the kinetic theory, which is also the basis of the theory of heat capacity treated above, is that the particles of an ideal gas can be considered as points or at least as tiny spheres. And it is exactly monatomic gases that correspond the closest to such a notion of a gas.

The mean energy of such a particle is completely determined by the mean kinetic energy of its *translational* motion $m\overline{v^2}/2$. This energy can be represented as the sum of three addends — the kinetic energies of motion of a molecule in three mutually perpendicular directions:

$$\frac{m\overline{v^2}}{2} = \frac{m\overline{v_x^2}}{2} + \frac{m\overline{v_y^2}}{2} + \frac{m\overline{v_z^2}}{2}$$

where $v_x$, $v_y$, and $v_z$ are the components of the velocity of the molecule along the three axes of coordinates. The completely chaotic nature of molecular movements permits us to consider that the mean values of the kinetic energies in the three directions are equal to one another:

$$\frac{m\overline{v_x^2}}{2} = \frac{m\overline{v_y^2}}{2} = \frac{m\overline{v_z^2}}{2} = \frac{1}{3}\,\frac{m\overline{v^2}}{2} \tag{2.15}$$

Since according to the basic equation of the kinetic theory, we have

$$\frac{m\overline{v^2}}{2} = \frac{3}{2} kT$$

then each of the three addends of Eq. (2.15) equals $kT/2$.

The division of the kinetic energy of a particle into three independent components is connected with the fact that a particle is considered as a free material point having *three degrees of freedom.*

It should be remembered that by the number of degrees of freedom of a mechanical system is meant the number of independent coordinates determining its position and configuration in space. Hence, an energy equal to $kT/2$ falls to the share of each degree of freedom of a monatomic molecule.

If, for example, a hypothetic gas existed whose molecules would be able to move only along a certain line (a one-dimensional gas), the mean kinetic energy of a molecule of such a gas would equal $kT/2$. The molar heat capacity at constant volume for such a gas would equal $R/2$ instead of $3R/2$. A two-dimensional gas, i.e. a gas whose molecules are limited in their motion by a plane, would have the heat capacity $C_V$ equal to $2R/2=R$.*

## 2.8. HEAT CAPACITY OF DIATOMIC AND POLYATOMIC GASES

Measurements conducted with diatomic and polyatomic gases showed that their molar heat capacities exceed those of monatomic gases. This can be seen from Table 6, in which the values of the same quantities as in Table 5 are given for a number of polyatomic gases.

*Table 6*

**Heat Capacity of Polyatomic Gases**

| Gas | $\frac{C_V}{R}$ | $\frac{C_p - C_V}{R}$ | $\gamma = \frac{C_p}{C_V}$ | Gas | $\frac{C_V}{R}$ | $\frac{C_p - C_V}{R}$ | $\gamma = \frac{C_p}{C_V}$ |
|---|---|---|---|---|---|---|---|
| Hydrogen ($H_2$) | 2.44 | 0.995 | 1.41 | Chlorine ($Cl_2$) | 3.02 | 1.09 | 1.36 |
| Hydrogen chloride (HCl) | 2.54 | 1.02 | 1.40 | Water (vapour, $H_2O$) | 3.3 | 1.06 | 1.32 |
| Nitrogen ($N_2$) | 2.45 | 1.005 | 1.404 | Carbon dioxide ($CO_2$) | 3.4 | 1.02 | 1.3 |
| Carbon monoxide (CO) | 2.48 | 1.005 | 1.404 | Ethylene ($C_2H_4$) | 4.04 | 1.03 | 1.25 |
| Oxygen ($O_2$) | 2.50 | 1.004 | 1.401 | Methane ($CH_4$) | 3.25 | 1.01 | 1.31 |
| Nitric oxide (NO) | 2.51 | 1.005 | 1.4 | Ammonia ($NH_3$) | 3.42 | 1.06 | 1.31 |

Examination of the table shows that gases whose molecules contain two or more atoms differ from monatomic gases in the values of the quantities $C_V/R$ (and, therefore, $C_V$) and $C_p/C_V$. The value of the expression ($C_p$ —

* A gas adsorbed on the surface of a solid approximately has the properties of a two-dimensional gas.

$-C_V)/R$ is the same for all gases. This means that regardless of the number of atoms in a molecule, the difference between the molar heat capacities always equals $R$, i.e. a mole of any ideal gas expanding at constant pressure when its temperature is increased by one kelvin performs the same work equal to $R$.

It can also be seen from the table that the gases listed in it can clearly be divided into two groups: diatomic gases for which $C_V/R$ is close to 2.5 and $C_p/C_V$ is close to 1.4, and gases whose molecules contain three and more atoms. For the latter, the values of $C_V/R$ are close to 3 and of $C_p/C_V$ close to 1.3.

This means that for gases of the first group (diatomic) the values of the molar heat capacities are close to one another and are as follows:

$$C_V = \frac{5}{2}R \approx 20.8 \text{ J/mol} \cdot \text{K} \approx 5 \text{ cal/mol} \cdot \text{K}$$

$$C_p = \frac{5}{2}R + R \approx 29.1 \text{ J/mol} \cdot \text{K} \approx 7 \text{ cal/mol} \cdot \text{K}$$

Consequently,

$$\frac{C_p}{C_V} \approx \frac{7}{5} = 1.4$$

For gases whose molecules consist of three or more atoms, the heat capacities, as can be seen from Table 6, have the following numerical values:

$$C_V = 3R \approx 24.9 \text{ J/mol} \cdot \text{K} \approx 6 \text{ cal/mol} \cdot \text{K}$$

$$C_p = 3R + R \approx 33.3 \text{ J/mol} \cdot \text{K} \approx 8 \text{ cal/mol} \cdot \text{K}$$

whence

$$\frac{C_p}{C_V} \approx \frac{8}{6} \approx 1.33$$

The experimental data on the heat capacity given above relate to gases at comparatively low pressures (of the order of magnitude of an atmosphere and below) and to temperatures close to room ones. In these conditions, gases only slightly differ from ideal.

How can we explain such laws relating to the values of the heat capacities of di- and polyatomic gases? The answer to this question is given by the so-called equipartition law.

**Equipartition Law and Heat Capacity of Polyatomic Gases.** On a preceding page when considering the heat capacity of a monatomic gas, we gave attention to the fact that the mean kinetic energy of a molecule per degree of freedom equals $kT/2$. It would be natural to assume that if a molecule of a gas had other degrees of freedom, the kinetic energy $kT/2$ would also fall to each of them.

Indeed, in classical statistical physics (classical means not quantum), such a theorem is proved (Boltzmann). It can be worded as follows: *if a*

*system of molecules is in thermal equilibrium at the temperature T, then the mean kinetic energy is uniformly distributed among all the degrees of freedom, and for each degree of freedom of a molecule it equals kT/2.*

(This law can also be worded in a different way: if a component of the energy of a system is proportional to the square of a coordinate or component of the velocity, then in a state of thermal equilibrium of the system at the temperature $T$ the mean value of this part of the energy equals $kT/2$.)

This theorem is called the law of uniform distribution of the kinetic energy among the degrees of freedom, or in short the *equipartition law*.

This law permits us to answer the question raised above.

With respect to their internal energy, di- and polyatomic gases differ from monatomic ones in the number of degrees of freedom of their molecules. Therefore, to calculate the internal energy of a gas and, consequently, its heat capacity, we have to know how to determine the number of degrees of freedom of the gas molecules.

Consider first the simplest case — a diatomic molecule. It can be imagined in the form of a system consisting of two atoms at a certain distance from each other (Fig. 34). If the distance between the atoms does not change (we shall call such molecules rigid), then this system, generally speaking, has six degrees of freedom.

Indeed, the position and the configuration of such a molecule are established by the three coordinates of its centre of mass, which determine the translational motion of the molecule as a whole, and by the three coordinates determining the possible rotations of the molecule about the mutually perpendicular axes $X$, $Y$, and $Z$.

Experiments and theory show, however, that rotation of molecules about the $X$-axis (see Fig. 34), on which the centres of both atoms are, can be excited only at very high temperatures. At ordinary temperatures, no rotation occurs about the $X$-axis, and a separate atom also does not rotate. Hence, two coordinates are sufficient for describing the possible rotations of our molecule.

Therefore, the number of degrees of freedom of a rigid diatomic molecule is five, of which three are translational and two are rotational degrees of freedom.

But the atoms in a molecule are not always rigidly bound to each other; they may vibrate relative to each other. Hence, still another coordinate is needed to determine the configuration of a molecule — the distance between the atoms.

Thus, in the general case, a diatomic molecule has *six* degrees of freedom: three translational, two rotational, and one vibrational.

If a molecule consists of $n$ atoms not bound together rigidly, it has $3n$ degrees of freedom (each atom has three degrees of freedom). Of this number, three degrees of freedom are translational and three are rotational,

except when the atoms are along a single straight line. Here there will only be two rotational degrees of freedom (as in a diatomic molecule).

For an example, Fig. 35 shows a model of a triatomic molecule and the axes $X$, $Y$, and $Z$ along which the vector of the angular velocity of the mole-

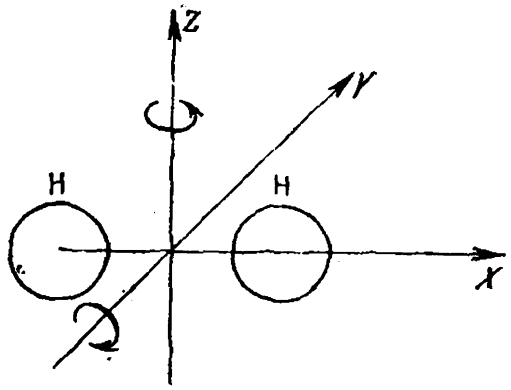



Fig. 34

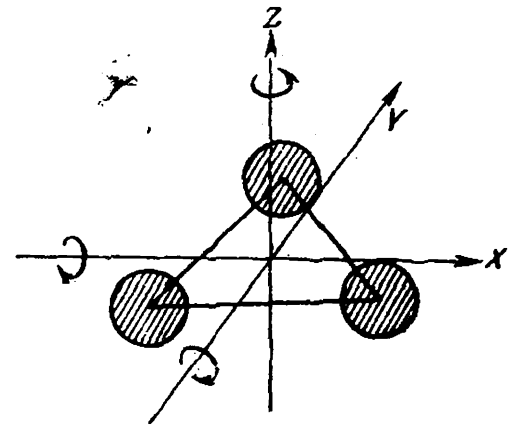



Fig. 35

cule can be resolved. Thus, a non-linear $n$-atomic molecule in the general case can have $3n - 6$ vibrational degrees of freedom, and a linear molecule $3n - 5$.

The vibrational motion of atoms is often not excited at all. But if the atoms in a molecule do vibrate and if the amplitudes of the vibrations are sufficiently small (in comparison with the distance between the atoms), such vibrations can be considered harmonic. The atoms in this case are harmonic oscillators.

An oscillator, however, has not only kinetic, but also potential energy (the latter is due to the force returning the atom to its equilibrium position). It is known from mechanics that for a *harmonic* oscillator the mean values of the kinetic and potential energy are equal. Therefore, if *harmonic* vibrations of the atoms are excited in a molecule, then according to the equipartition law $kT/2$ falls to each vibrational degree of freedom in the form of kinetic energy and $kT/2$ in the form of potential energy. This does not hold for anharmonic vibrations.

In other words, the energy falling to each *vibrational* degree of freedom is not $kT/2$, but $2 \times kT/2 = kT$.

Now it is not difficult to calculate the heat capacity of polyatomic gases.

If the number of degrees of freedom of a molecule of a gas is $i$, then its mean energy is $i(kT/2)$, and the internal energy of one mole of such a gas is

$$U = \frac{i}{2} RT \tag{2.16}$$

Accordingly, the molar heat capacities of the gas are

$$C_V = \frac{dU}{dT} = \frac{i}{2} R \tag{2.17}$$

and

$$C_p = C_V + R = \left(\frac{i}{2} + 1\right) R \tag{2.18}$$

In calculating the number of degrees of freedom $i$, the number of vibrational degrees of freedom has to be doubled. This may not be done if we give a somewhat different definition of the number of degrees of freedom $i$, namely, if this number is defined as *the number of independent quadratic variables by which the energy of a system is determined.*

Indeed, the kinetic energy of the translational and rotational motions of a molecule is proportional to the sum of the *squares* of the relevant (independent) components of the velocities (linear and angular).

As regards the energy of the vibrations of the atoms inside a molecule, performed, for instance, along the $X$-axis, it equals the sum of the kinetic energy, which is proportional to the *square* of the velocity $(dv_x/dt)^2$, and the potential energy, which is known to be proportional to $x^2$, the *square* of the displacement $x$ relative to the position of equilibrium. Thus, according to the new definition of the number of degrees of freedom, two degrees of freedom should be assigned to vibrational motion of an atom along a given axis, and Eq. (2.16) can be employed without any reservations (compare the second wording of the equipartition law).

The above considerations on the possible number of degrees of freedom of molecules permit us to interpret the experimental data on the heat capacity of polyatomic gases given in Table 6.

For example, from the fact that the heat capacity of hydrogen, nitrogen, oxygen, and some other diatomic gases equals $5R/2$ quite accurately, it follows that the number of degrees of freedom of the molecules of these gases equals 5. This means that molecules of these gases can be considered rigid (the vibrational degrees of freedom are not excited). The same relates to some triatomic gases. But here the experimental results show appreciable deviations from the theoretically expected ones. It follows from Eq. (2.17) that the heat capacity $C_V$ for "rigid" triatomic molecules should equal $6R/2 = 3R$. However, the heat capacities of all the triatomic gases listed in Table 6 are somewhat greater than this value (by an amount which cannot be explained by the errors of measurement).

An attempt to explain the found values of the heat capacity of chlorine from the viewpoint of the above theory also encounters difficulties. The value of the heat capacity of chlorine given in Table 6, i.e. $C_V = 3.02R$, corresponds to six degrees of freedom for a chlorine molecule. But the latter, being diatomic, can have either five degrees of freedom if its two atoms are rigidly bound to each other (hence, $C_V = 5R/2$), or seven degrees of freedom (according to the second definition of the number $i$) if the atoms inside a molecule may vibrate (hence, $C_V = 7R/2$).

Hence, in this case too, the theory of heat capacity cannot be considered satisfactory. The explanation is that our theory is not in a position to

take due account of the energy connected with internal motions in a molecule to which the equipartition law cannot always be applied.

An especially important deviation from the results of theory is the fact that the heat capacity has been found to depend on the temperature. According to Eq. (2.17), however, it should be a constant quantity for a given gas with a given value of $i$. Experiments show that the heat capacity diminishes with decreasing temperature.

One explanation of this relationship could be that a change in the temperature is attended by a change in the number of "acting" degrees of freedom of the molecules, i.e. certain movements of the molecules occurring in one region of temperatures cease in another. Such an assumption, however, requires the heat capacity to change in jumps with the temperature. A certain movement may either occur or not occur. In the former case, the energy $kT/2$ corresponds to it. In the latter, this energy and the contribution to the heat capacity connected with it are absent. A gradual change in the intensity of a certain kind of movement of a molecule is naturally possible instead of its suddenly stopping or appearing. But the equipartition law does not distinguish this. The same energy is connected with any degree of freedom*. At the same time, our experience shows that the temperature dependence of the heat capacity is a smooth curve — the heat capacity changes gradually. This indicates that the equipartition law governing the distribution of energy among the various degrees of freedom cannot be considered entirely true and has a limited applicability.

**Heat Capacity of Hydrogen.** Hydrogen is distinguished by an especially sharply expressed temperature dependence of the heat capacity. At room temperature, the heat capacity of hydrogen at constant volume equals 5 cal/mol·K, while at about 50 K (−223 °C) it becomes equal to 3 cal/mol·K, i.e. hydrogen behaves like a monatomic gas having three degrees of freedom.

The temperature dependence of the heat capacity of hydrogen is shown in Fig. 36, from which it can be seen that the heat capacity diminishes gradually with decreasing temperature. Generally speaking, this cannot be explained from the standpoint of the classical theory of heat capacity. True, it can be assumed that lowering of the temperature is attended by a gradual reduction in the number of molecules performing rotational motion. But in this case, it again remains unclear why only one part of the molecules performs such motion whereas in the other part these degrees of freedom remain "disengaged".

Here we have encountered one of the many cases when classical physics is not able to explain experimental facts. The divergence of theory and experimental data obviously indicates that our notion of molecules as rigid spheres whose movements follow the laws of mechanics does not completely correspond to actual facts. Molecules are now well known to consist of

* As A. Sommerfeld aptly put it, "degrees of freedom are counted, and not assessed".

atoms interacting with one another. The atoms have an intricate structure and consist of numerous still smaller particles that also move in a complicated fashion. The motion of the atomic particles, however, does not

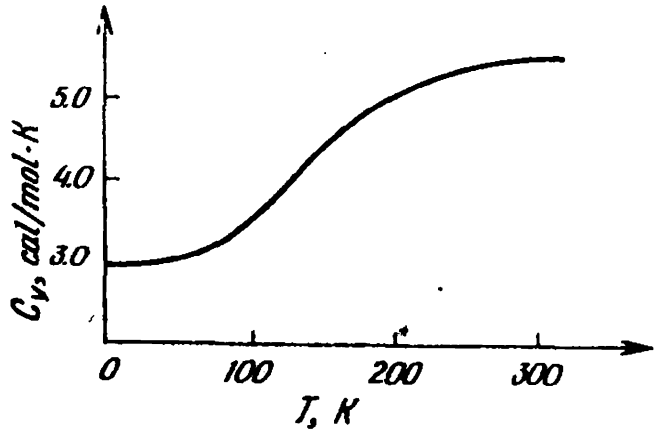



Fig. 36

obey the laws of classical mechanics, but is governed by a special "code of laws" — quantum mechanics. Therefore, as long as we are dealing with the heat capacity of monatomic gases that are not affected by intratomic movements and the energy connected with them, the heat capacity theory set out above excellently agrees with experimental facts. But in polyatomic molecules, an appreciable part is already played by internal processes in the molecules and atoms with which the vibrational degrees of freedom, for example, are undoubtedly related. It is therefore quite natural that our theory, which takes no account of the special quantum properties of atomic systems, in this case gives only approximately true results. The quantum theory, on the other hand, gives a complete explanation of all the experimental data on heat capacity.

Particularly, for a hydrogen atom, the quantum theory shows that hydrogen molecules can be in two different states — *para-hydrogen* and *ortho-hydrogen*, whose heat capacities should differ from each other. The difference between these states is as follows.

The quantum theory teaches that atoms (more exactly, atomic nuclei) have a certain angular momentum (moment of momentum). When a molecule is formed from two atoms of hydrogen, these momenta of the nuclei (like any other momenta, they are vectors) may be either parallel ( $\uparrow\uparrow$ ) or antiparallel ( $\downarrow\uparrow$ ) to each other. Both the existence itself of the nuclear momenta and their possible orientations are a corollary of quantum mechanics and cannot be obtained from conventional mechanics. Hydrogen whose molecules consist of atoms with parallel nuclear momenta is called *ortho*-hydrogen, unlike hydrogen with antiparallel momenta of the atomic nuclei in a molecule, which is called *para*-hydrogen.

Ordinary hydrogen contains both kinds of molecules, their relative content depending on the temperature. At room temperature, normal hydrogen contains about 25% of *para*-hydrogen. Lowering of the

temperature is attended by a growth in its content so that at 20 K hydrogen consists almost completely of *para*-hydrogen (99.8%).*

Different values of the energy of rotational motion correspond to the *ortho*- and *para*-states of hydrogen. This explains the different values of its heat capacity in these two states. At low temperatures (about 50 K), however, the heat capacity depending on the rotational motion of the molecules in both states becomes equal to zero. This is exactly why the heat capacity of hydrogen becomes the same as for a monatomic gas.

The heat capacity of other polyatomic gases, like that of hydrogen, drops with lowering of the temperature and tends to the value of the heat capacity of monatomic gases ($3R/2$). This occurs, however, in the region of very low temperatures when the direct measurement of the heat capacity of gases encounters great difficulties.

Measurements of the heat capacity thus permit us to arrive at important conclusions on the structure of molecules. Therefore, such measurements, especially at low temperatures, are of a great significance. In addition, we must know the value of the heat capacity and its temperature dependence in solving many technical problems.

## 2.9. CHANGE IN STATE WHEN VOLUME OF A GAS CHANGES

From Eq. (2.9) of the law of conservation of energy

$$dQ = C_V\, dT + p\, dV$$

we can see that the heat supplied to a gas can cause a change in its temperature ($dT$) and its volume ($dV$). In the preceding sections, we considered the process of a change in the temperature of a gas from the energy viewpoint. Now we shall turn to considering the expansion and compression of an ideal gas, i.e. the change in its state when the volume changes.

It was shown that the quantity of heat needed to change the temperature of a gas depends on the conditions in which this change occurs, and on whether the volume or pressure of the gas remains constant when it is heated, i.e. whether the change in the temperature is isochoric or isobaric.

The compression and expansion of a gas can also occur in different conditions. The energy result of a process, i.e. the *work done during it* (we know that the change in the volume of a gas is connected with work), depends on its conditions.

The compression and expansion of a gas can be conducted so that its temperature remains constant. Such a process is called *isothermal*. It can be carried out by placing the gas in a vessel provided with a piston, the temperature of the vessel being kept constant. For this purpose, it is placed in a thermostat — an apparatus provided with a source of energy (an electri-

* The transition of molecules from the *ortho*- to the *para*-state proceeds very slowly at ordinary temperatures. It accelerates when the hydrogen comes into contact with certain metals.

cal stove, a heater, etc.). When good contact is provided between the gas and the medium of the thermostat, constancy of the temperature can be achieved by diminishing the quantity of heat supplied from the source when the gas liberates energy, and by increasing the quantity of heat when the gas absorbs energy. A special device — a *thermoregulator* — automatically maintains a constant temperature in the thermostat.

If in these conditions we move the piston (see Fig. 31) downward with the aid of an external force, the gas will be compressed, and the external force will perform work. Conversely, in expansion, positive work is done by the force with which the gas presses on the piston.

The volume can also be changed in conditions when no heat is supplied to a gas or removed from it. Such a process is called *adiabatic*. Unlike an isothermal process which requires good contact with the medium of the thermostat, an adiabatic process requires careful thermal insulation of the gas from the surroundings.

## 2.10. WORK IN ISOTHERMAL CHANGE IN VOLUME OF AN IDEAL GAS

To determine the work in an isothermal change in the volume of a gas, we must, according to Eq. (2.4), calculate the integral

$$\int dW = \int p\, dV$$

along the isotherm. We cannot carry $p$ out from under the integral sign because the pressure continuously changes in expansion. It changes together with a change in the volume according to Boyle's law, i.e.

$$pV = RT = \text{const}, \text{ whence } p = \frac{RT}{V}$$

Inserting this expression for $p$ under the integral sign, we get the work $W$ when the volume changes from $V_1$ to $V_2$:

$$W = \int_{V_1}^{V_2} RT \frac{dV}{V} = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln \frac{V_2}{V_1} \tag{2.19}$$

This is the expression for the work of isothermal expansion (or compression) of one mole of an ideal gas. If the mass of the gas is not one mole, Eq. (2.19) becomes

$$W = \frac{M}{\mu} RT \ln \frac{V_2}{V_1} \tag{2.20}$$

where $M/\mu$ is the number of moles.

Inspection of Eqs. (2.19) and (2.20) shows that the work of isothermal expansion depends on the ratio of the volumes after and before expansion (and not on their difference). The same naturally holds for compression.

Since according to Boyle's law we have $p_1V_1 = p_2V_2$, then

$$\frac{V_2}{V_1} = \frac{p_1}{p_2}$$

Therefore, in Eqs. (2.19) and (2.20) we can substitute the inverse ratio of the pressures for the ratio of the volumes. Hence,

$$W = \frac{M}{\mu} RT \ln \frac{p_1}{p_2} \tag{2.21}$$

As noted above, in isothermal expansion, the heat supplied to a gas is used only for performing external work. Conversely, in isothermal compression, the work of external forces goes to increase the internal energy (heat) of the surrounding bodies. Formally, this corresponds to the fact that the heat capacity of a gas $dQ/dT$ equals $\infty$ (because $dT = 0$).

## 2.11. ADIABATIC CHANGE IN VOLUME OF AN IDEAL GAS

In an adiabatic process, a gas does not give up heat to its surroundings, and does not receive heat from them ($dQ = 0$). Here the law of conservation of energy becomes

$$-p\,dV = C_V\,dT \tag{2.22}$$

This means that the work connected with a change in the volume of a gas must be attended by a change in internal energy and, consequently, in temperature. The minus sign in Eq. (2.22) means that an increase in the volume of a gas (expansion) is accompanied by a drop in its temperature, and compression by an increase in its temperature. In the first case, work is done by the gas at the expense of its own internal energy, and this is why its temperature lowers. In the second case, work is done by an external force. This work causes the internal energy and, consequently, the temperature of the gas to grow.

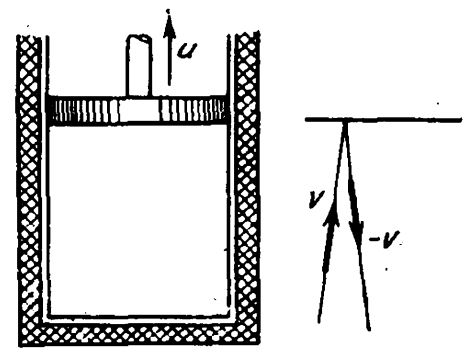


Fig. 37

It is easy to imagine the "kinetic" picture of this temperature change. Suppose we have a vessel with a gas in the form of a cylinder with a piston (Fig. 37). Assume further that the piston rises with the velocity $u$ (the gas is expanding). Consider a molecule travelling with the velocity $v$ in the same direction as the piston. If the velocity of this molecule "catching up" with the

piston is $v$ relative to the walls of the vessel, then it is $v - u$ relative to the piston. After our molecule has "caught up" with the piston and an elastic collision has occurred, its velocity relative to the piston should as previously remain equal to $v - u$, although now it is moving away from the piston instead of following it. This means that its velocity relative to the walls of the vessel should be less than previously by the value $v - 2u$. Hence, all the molecules colliding with the moving piston are reflected from it with a lower velocity than that before the collision. This results in a drop in the mean velocity of the molecules and, therefore, in a decrease in the temperature.

The temperature should rise in the same way when the piston moves in the reverse direction.

**Poisson Equation.** Before calculating the work done in an adiabatic change in the volume of a gas, we must find the relationship between the volume of the gas and its pressure because in an adiabatic process it will no longer be determined by Boyle's law. For this purpose, we must exclude $T$ from the equation

$$C_V\, dT + p\, dV = 0 \tag{2.23}$$

This can be done by using the equation of state (1.11): $pV = RT$. Its differentiation yields

$$p\, dV + V\, dp = R\, dT$$

whence

$$dT = \frac{p\, dV + V\, dp}{R} \tag{2.24}$$

Substituting for $dT$ in Eq. (2.23) its value from Eq. (2.24), we get

$$C_V \frac{p\, dV + V\, dp}{R} + p\, dV = 0$$

or after using instead of $R$ its value $C_p - C_V$ (see Sec. 2.6), we have

$$C_V\, V\, dp + C_p\, p\, dV = 0 \tag{2.25}$$

Since $C_p/C_V = \gamma$, Eq. (2.25) becomes

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0 \tag{2.26}$$

Assuming that $\gamma$ is constant, we can write

$$\int \frac{dp}{p} + \gamma \int \frac{dV}{V} = 0$$

Integration yields $\ln p + \gamma \ln V = \text{const}$, or

$$pV^{\gamma} = \text{const} \tag{2.27}$$

This is the required relationship between the pressure and the volume of an ideal gas in an adiabatic process of a change in volume.

Equation (2.27) is called the *Poisson equation* or the *equation of an adiabat*, and the quantity $\gamma = C_p/C_V$ — the *adiabatic exponent*.

When integrating Eq. (2.26), we assumed that the quantity $\gamma$ is constant. Strictly speaking, this is not completely accurate. The heat capacity $C_V$, and, therefore, $C_p$ and $\gamma$ may change with a change in the volume, pressure, and temperature. Hence, the Poisson equation (2.27) strictly holds for a limited interval of pressures and volumes. The differential equation (2.26) is accurate.

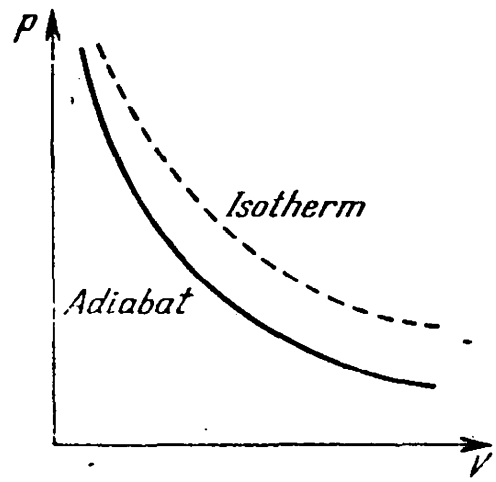


Fig. 38

It can be seen from the Poisson equation that unlike an isothermal process, in an adiabatic change in the volume of a gas its pressure changes inversely proportional to $V^{\gamma}$ instead of to the first power of the volume. The value of $\gamma$ is greater than unity because $C_p > C_V$. Hence, the graph of pressure against volume will no longer be a hyperbola.

Since $\gamma > 1$, the curve $p = f(V)$ for an adiabatic process, called an *adiabat*, is steeper than an isotherm. This can be seen from Fig. 38, which shows an adiabat and for comparison an isotherm of an ideal gas. The steeper drop in pressure with an increase in volume in an adiabatic process is explained by the fact that the pressure of an ideal gas in adiabatic expansion diminishes not only at the expense of an increase in the volume, but also owing to a drop in the temperature of the gas.

It is not difficult to find the relationships between the other parameters of a gas in an adiabatic process.

For example, to find the relationship between the temperature and volume of a gas in an adiabatic change, we use the value of $p = RT/V$ obtained from Eq. (1.11) in Eq. (2.27). We get

$$\frac{RT}{V} V^{\gamma} = \text{const}$$

or

$$TV^{\gamma-1} = \text{const} \tag{2.28}$$

(because $R$ is a constant quantity).

Similarly, from Eq. (1.11) we have $V = RT/p$, and, after substitution in Eq. (2.27), we get the relationship between the pressure and temperature of a gas in an adiabatic process:

$$p\left(\frac{RT}{p}\right)^{\gamma} = \text{const}$$

or

$$T^{\gamma} p^{1-\gamma} = \text{const} \tag{2.29}$$

*By raising both sides of Eq. (2.29) to the power* $1/\gamma$, we have

$$Tp^{\frac{1-\gamma}{\gamma}} = \text{const} \tag{2.30}$$

The remark on the limits of applicability of the Poisson equation naturally also relates to Eqs. (2.28) and (2.30).

## 2.12. WORK IN ADIABATIC CHANGE IN VOLUME OF A GAS

Using the equation of an adiabat (2.27), we can now calculate the work done by a gas upon its adiabatic expansion (or the work done by external forces in compression of a gas).

Let us calculate the work of expansion of one mole of a gas from the initial volume $V_1$ to $V_2$. As previously, the elementary work upon a change in the volume by $dV$ is

$$dW = p\,dV \tag{2.31}$$

The relationship between the pressure of the gas $p$ and its volume $V$ is determined by Eq. (2.27) (to be an equilibrium one, the process of expansion must be conducted along an adiabat):

$$pV^{\gamma} = \text{const}$$

which we can also rewrite in the form

$$pV^{\gamma} = p_1 V_1^{\gamma}$$

where $p_1$ and $V_1$ are the initial pressure and volume of the gas, respectively. Hence,

$$p = \frac{p_1 V_1^{\gamma}}{V^{\gamma}}$$

Introducing this value of $p$ into Eq. (2.31), we get

$$dW = \frac{p_1 V_1^{\gamma}}{V^{\gamma}}\,dV$$

To find the work of expansion from $V_1$ to $V_2$, we have to integrate the expression for $dW$ within this interval:

$$W = \int_{V_1}^{V_2} p_1 V_1^{\gamma} \frac{dV}{V^{\gamma}} = p_1 V_1^{\gamma} \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

After integration, we get the following expression for the integral in the right-hand side of the equation:

$$\int_{V_1}^{V_2} \frac{dV}{V^\gamma} = \frac{1}{\gamma - 1}\left(\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right)$$

Therefore, the expression for the work $W$ becomes

$$W = \frac{p_1 V_1^\gamma}{\gamma - 1} \frac{1}{V_1^{\gamma-1}}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right]$$

It follows from the equation of state (1.11) that $p_1 = RT_1/V_1$, whence we get the final expression

$$W = \frac{RT_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \tag{2.32}$$

If the mass of a gas is $M$, Eq. (2.32) becomes

$$W = \frac{M}{\mu}\frac{RT_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \tag{2.33}$$

Since $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$, then $\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1}$. Therefore, the equation for the work done in the adiabatic change in the volume can be written in the form

$$W = \frac{RT_1}{\gamma - 1}\left(1 - \frac{T_2}{T_1}\right) = \frac{R}{\gamma - 1}(T_1 - T_2) = C_V(T_1 - T_2)$$

because $R/(\gamma - 1) = C_V$.

A comparison of Eqs. (2.32) and (2.20) shows that less work is done in adiabatic expansion than in isothermal (with the same change in volume). This is connected with the greater steepness of an adiabat in comparison with an isotherm because, the initial conditions being the same, the pressure in an adiabatic process will be less than in an isothermal one at any stage of expansion.

The work in the adiabatic expansion of a gas depends appreciably on the value of the adiabatic exponent $\gamma = C_p/C_V$. It is easy to see that if $\gamma \to 1$, the work of adiabatic expansion tends to the value of the work in an isothermal process. This can be proved by finding the limiting value of the right-hand side of Eq. (2.32) for $\gamma \to 1$ (using the l'Hospital rule).

The value of $\gamma$ is the closest to unity for polyatomic gases, and the difference between the values of the work in an isothermal and an adiabatic processes is the smallest for them.

It is the most convenient to compare the two processes considered above by using a graph showing the change in the volume of a gas. In a graph showing the pressure of a gas against its volume (Fig. 39), the elementary

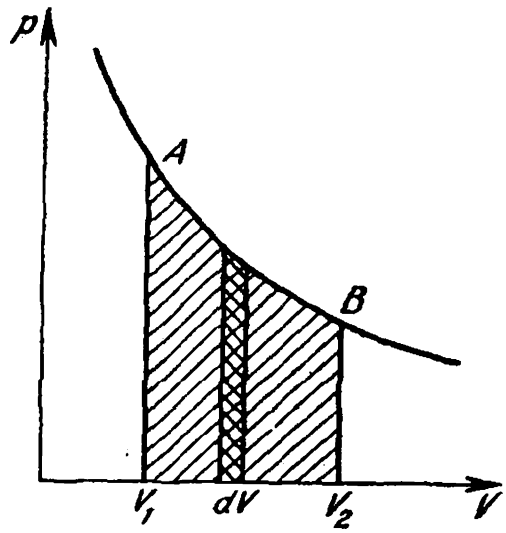



Fig. 39

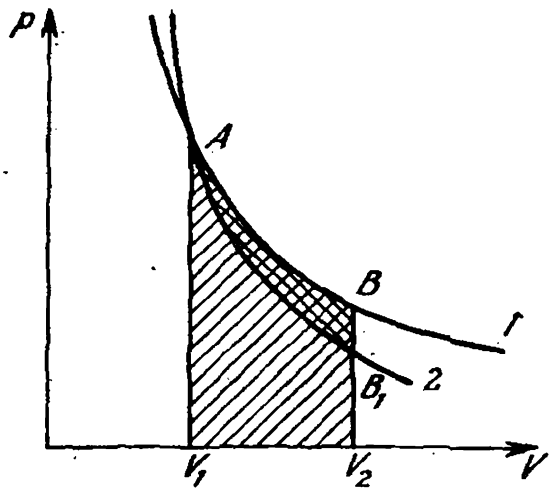



Fig. 40

work $dW$ for changing the volume of the gas by $dV$ is depicted by the area confined by part of curve $AB$ and the length $dV$ on the axis of abscissas (the cross-hatched area). The work done to change the volume of the gas from $V_1$ to $V_2$, equal to $\int_{V_1}^{V_2} p\,dV$, is depicted by the entire hatched area confined by the relevant part of curve $AB$ and the length $V_1V_2$ on the axis of abscissas.

Figure 40 gives for purposes of comparison curves *1* and *2* which are an isotherm and an adiabat for the same gas and the same initial conditions. The work of isothermal change in the volume of the gas from $V_1$ to $V_2$ equals area $ABV_2V_1A$ while the corresponding work of adiabatic expansion equals area $AB_1V_2V_1A$ which is obviously smaller (see Fig. 40).

The smaller the adiabatic exponent $\gamma$, the closer is the adiabat to an isotherm and the smaller is the difference between the areas under the two curves. In the limit, when $\gamma \to 1$, the adiabat transforms into an isotherm.

## 2.13. POLYTROPIC PROCESS

The isothermal and adiabatic processes of the change in the state of a gas considered above are idealized processes. The first of them requires ideal contact with the surroundings or a thermostat, the second — just as ideal isolation. Both these processes can be considered as special extreme cases of a more general process called *polytropic*. This is the name given to

any process of the change in state when the heat capacity $C$ remains constant and equal to $dQ/dT$:

$$C = \frac{dQ}{dT} \text{ or } dQ = C\,dT$$

Let us find the general equation for a polytropic process (the *equation of a polytrope*).

According to the first law of thermodynamics,

$$dQ = C\,dT = C_V\,dT + p\,dV$$

or

$$(C - C_V)\,dT = p\,dV \tag{2.34}$$

Using Eq. (2.24), i.e.

$$dT = \frac{p\,dV + V\,dp}{R}$$

in (2.34) and substituting $C_p - C_V$ for $R$, we get

$$\frac{C - C_V}{C_p - C_V}(p\,dV + V\,dp) = p\,dV$$

whence

$$\left(\frac{C - C_V}{C_p - C_V} - 1\right)p\,dV = -\frac{C - C_V}{C_p - C_V}V\,dp$$

After separating variables and performing simple transformations, we obtain

$$\frac{C - C_p}{C_p - C_V}\frac{dV}{V} = -\frac{C - C_V}{C_p - C_V}\frac{dp}{p}$$

Integration of this equation yields

$$\ln p + \frac{C - C_p}{C - C_V}\ln V = \text{const}$$

Introducing the notation

$$\frac{C - C_p}{C - C_V} = n \tag{2.35}$$

we get

$$pV^n = \text{const} \tag{2.36}$$

The exponent $n$ in this equation, determined by Eq. (2.35), where $C$ is the heat capacity of the gas in the given process, is called the *polytropic*

*exponent*. For an adiabatic process for which the heat capacity $C$ equals zero (because $dQ = 0$), the exponent $n = C_p/C_V = \gamma$. For an isothermal process for which the heat capacity equals infinity (because $dT = 0$), the exponent $n$ equals unity.

If in Eq. (2.35) we assume that the heat capacity $C = C_p$, then from Eq. (2.36) we get $p = \text{const}$. If we assume in Eq. (2.35) that $C = C_V$ so that $n$ becomes equal to $\infty$, we get $V = \text{const}$. This can easily be seen if we raise Eq. (2.36) to the power $1/n$.

**Adiabatic Compressibility of an Ideal Gas.** It was shown in Sec. 1.5 [Eq. (1.14)] that the isothermal compressibility of an ideal gas $\varkappa$ equals $-1/p$. If we change the pressure of a gas in adiabatic conditions, its compressibility will be different. This is connected with the fact that in the adiabatic change of the pressure not only the volume changes, but also the temperature, which by itself affects the volume. Thus, if we increase the pressure, i.e. compress a gas, it becomes heated. This heating causes the volume of the gas to grow, which partly compensates for the reduction in volume due to compression.

It is therefore obvious from qualitative considerations that the compressibility of a gas upon an adiabatic change in pressure should be lower than the isothermal compressibility.

The value of the adiabatic compressibility, which by definition equals

$$\varkappa_a = \frac{1}{V}\frac{dV}{dp} \tag{2.37}$$

is obtained quantitatively directly from Eq. (2.26):

$$\varkappa_a = -\frac{1}{\gamma p} \tag{2.38}$$

The adiabatic compressibility of a gas is thus $\gamma$ times less than the isothermal compressibility.

## 2.14. EXPANSION OF A GAS INTO A VACUUM

Our reasoning on the heat processes in gases was based on the law of conservation of energy, expressed by Eq. (2.5):

$$dQ = dU + p\,dV$$

Indeed, a gas that is, for example, in a vessel with a movable piston exerts a pressure on the latter and upon expansion does work. In an isothermal process, the work is done at the expense of the heat supplied from the surroundings, in an adiabatic process, at the expense of the internal energy. In the latter case, expansion of the gas is attended by its cooling. Instead of the energy lost by the molecules, we get the kinetic energy of the piston if it receives a noticeable velocity, or potential

energy if, for example, a weight is lifted together with the piston or a spring is compressed. This energy can be used to bring an engine into motion if it is properly connected to the piston.

In adiabatic compression, on the contrary, the internal energy of a gas grows at the expense of the work of external forces. The energy of the body doing this work diminishes.

It must be noted, however, that the expansion of a gas alone cannot result in its cooling if no work is done during this expansion. This means that if an ideal gas is allowed to expand by connecting an empty vessel to the one it is in, its temperature will not change. Upon such *expansion into a vacuum*, an ideal gas does no work.

The constancy of the temperature of the gas in this case follows from the fact that the internal energy of an ideal gas does not depend on the volume it occupies. This was proved experimentally back in last century (1845) by J. Joule.

Joule's experiment consisted in the following. Two cylinders, one filled with air to a comparatively high pressure (about 20 atmospheres) and the other empty (evacuated) could be connected to each other with the aid of a cock. Both cylinders were placed in a water calorimeter, and the latter was insulated thermally from the surroundings with great care. In a certain time after the connecting cock had been opened, the change in the temperature of the water in the calorimeter was measured. The experiment showed that the temperature of the calorimeter did not change. This proved that the gas retained its initial temperature.

Joule's experiment can also serve as a proof of the fact that the internal energy of a gas (ideal) does not depend on the volume at constant temperature.

Later more accurate experiments showed that upon the expansion of a greatly compressed gas into a vacuum the temperature of the gas changes. But this change of temperature, as will be shown in Chap. 8, is connected with the non-ideal nature of the gas.

In the nineteenth century, when the kinetic theory was not yet developed sufficiently, much effort was spent to prove experimentally the truth of Eq. (2.3). After its truth had been established reliably, it was named the first law of thermodynamics.

From the viewpoint of the kinetic theory, according to which heat energy is the energy of chaotic movements of molecules, the first law of thermodynamics is simply an expression of the law of conservation of energy.

## 2.15. MEASUREMENT OF THE QUANTITY OF HEAT AND HEAT CAPACITY

**On Units of the Quantity of Heat.** Above we defined the unit of the quantity of heat — the calorie — as the quantity of heat needed to raise the temperature of one gramme of water by one kelvin at atmospheric pressure.

But since the heat capacity of water at different temperatures is different, we must come to an agreement on the temperature at which this interval of one kelvin is selected.

In the USSR, the so-called twenty degree calorie is used, corresponding to the interval from 19.5 to 20.5 °C. It equals 4.181 J. In some countries, the fifteen degree calorie is used, corresponding to the interval from 14.5 to 15.5 °C. It equals 4.184 J. This calorie, also called the mean calorie or the thermochemical calorie, equals one-hundredth of the quantity of heat needed to heat one gramme of water from 0 to 100 °C. It is sometimes designated $\text{cal}_{\text{th}}$ to distinguish it from the international thermal calorie, which by definition equals 4.1868 J and is designated $\text{cal}_{\text{IT}}$.

**Measurement of the Quantity of Heat.** Special devices called *calorimeters* are used for the direct measurement of the quantity of heat given up or received by a body.

The simplest calorimeter is a vessel filled with a substance whose heat capacity is well known, for example with water (its specific heat capacity is 1 cal/g·K).

The quantity of heat being measured is in some way or other transmitted to the calorimeter and causes its temperature to change. After measuring this change in temperature $\Delta T$, we get the heat $Q$:

$$Q = cm\,\Delta T$$

where $c$ = specific heat capacity of the substance filling the calorimeter
$m$ = its mass.

It must not be forgotten that heat is transmitted not only to the substance filling the calorimeter, but also to the vessel and various devices that may be placed in it. Hence before measurement, we must determine the so-called heat equivalent of the calorimeter—the quantity of heat needed to heat the "empty" calorimeter by one kelvin. Sometimes this correction is introduced by adding to the mass of the water $m_1$ an additional mass $m^*$ whose heat capacity equals the heat capacity of the vessel and other parts of the calorimeter. We can thus consider that heat is transmitted to a mass of water equal to $M = m_1 + m^*$. The quantity $M$ is called the water equivalent of the calorimeter.

**Measurement of Heat Capacity.** A calorimeter is also used to measure heat capacity. In this case, we must know exactly the quantity of supplied (or removed) heat $Q$. When the latter is known, the specific heat capacity is calculated by the equation

$$c = \frac{Q}{m\Delta T}$$

where $m$ = mass of the body being studied
$\Delta T$ = change in its temperature caused by the heat $Q$.

Heat is supplied to a body in a calorimeter which should be designed so that the heat is transmitted only to the body being studied (and, of

course, to the calorimeter) and is not lost to the surroundings. Such losses of heat always occur, however, and taking them into account is the main care in calorimetric measurements.

Measurement of the heat capacity of gases is difficult because owing to their low density the heat capacity of the portion of a gas that can be accommodated in a calorimeter is small. At ordinary temperatures, it may be comparable with the heat capacity of the empty calorimeter, which inevitably lowers the accuracy of measurements. This relates particularly to measurements of the heat capacity at constant volume $C_V$. In determining $C_p$, this difficulty can be circumvented if the gas being studied is made to flow (at constant pressure) through a calorimeter (see below).

**Measurement of $C_V$.** Virtually the only method for direct measurement of the heat capacity of a gas at constant volume is that proposed by P. Joly (1889). This method is shown schematically in Fig. 41.

The calorimeter consists of chamber $C$ in which two identical hollow copper spheres $S_1$ and $S_2$ are suspended from the ends of the beam of precise balance $B$. The spheres are provided with plates at the bottom and reflectors on top. One of the spheres is evacuated, and the other is filled with the gas to be studied. For the gas to have an appreciable heat capacity, it is introduced at a considerable pressure (up to 20 atm). The mass $M$ of the introduced gas is determined with the aid of the balance, by restoring the equilibrium violated by the introduction of the gas with the aid of weights.

After thermal equilibrium has set in between the spheres and the chamber, steam is admitted into the chamber (the pipes for the admission and exhaust of the steam are in the front and rear walls of the chamber and are not shown in Fig. 41). The steam condenses on both spheres, heats them, and flows down into the plates. But more water condenses on the sphere filled with the gas because its heat capacity is greater. Owing to the greater amount of condensate on one of the spheres, their equilibrium is again violated. After bringing the balance into equilibrium, we shall know the surplus mass of the water which condensed owing to the presence of the gas in one of the spheres. If this surplus mass of the water is $m$, then multiplying it by the heat of condensation of water $L$, we find the quantity of heat used to heat the gas from the initial temperature $T_1$ to the temperature of the steam $T_2$. After measuring these temperatures with a thermometer, we get

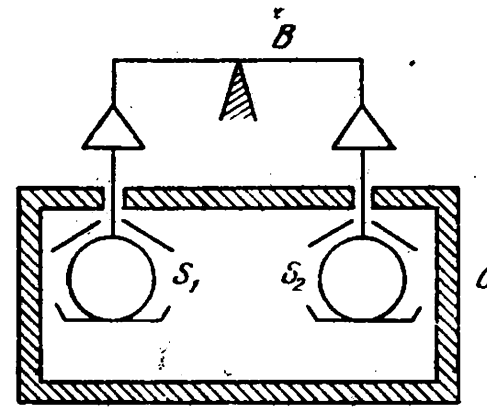


Fig. 41

$$mL = Mc_V(T_2 - T_1)$$

where $c_V$ is the specific heat capacity of the gas. Knowing $c_V$, we can calculate the molar heat capacity $C_V = \mu c_V$.

**Measurement of $C_p$.** We have already mentioned that to measure the heat capacity at constant pressure the gas being studied is made to flow through a calorimeter. Only in this way can we ensure a constant pressure

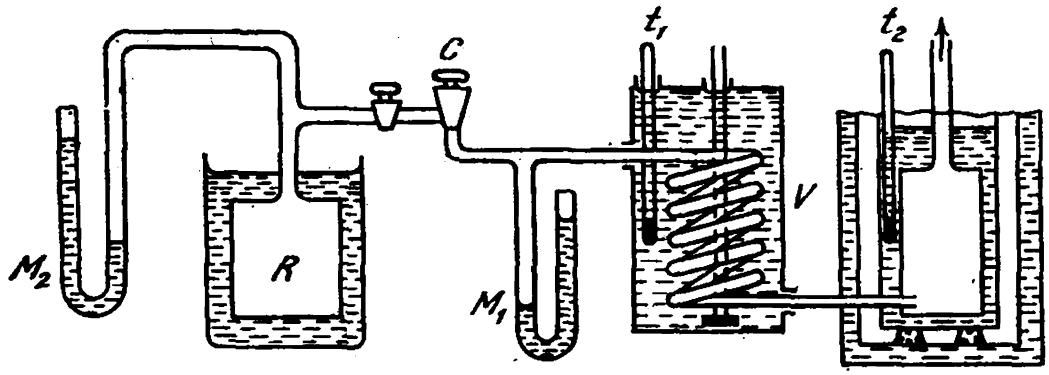



Fig. 42

of the gas, notwithstanding the supply of heat and heating without which the heat capacity cannot be measured. We shall describe the classical experiment conducted by H. Regnault (1862) as an example of such a method. A schematic view of the apparatus is shown in Fig. 42.

The gas being studied is passed from reservoir $R$ through cock $C$ into a coil placed in vessel $V$ with oil that is heated by some means or other. The pressure of the gas is regulated by cock $C$ to keep it constant, this being controlled by manometer $M_1$. After travelling a long path through the coil, the gas acquires the temperature of the oil, which is measured by thermometer $t_1$.

The gas heated in the coil then passes through a water calorimeter and is cooled in it to a certain temperature $T_2$ measured by thermometer $t_2$ and flows out. By measuring the pressure of the gas in reservoir $R$ at the beginning and the end of the experiment by means of manometer $M_2$, we find the mass $M$ of the gas that has passed through the apparatus.

The quantity of heat $Q$ given up by the gas to the calorimeter equals the product of the water equivalent $m$ of the calorimeter and the change in its temperature $T_2 - T_1$, where $T_1$ is the initial temperature of the calorimeter:

$$Q = m(T_2 - T_1)$$

On the other hand, the heat given up by the gas equals the product of its mass, the specific heat capacity, and the change in the temperature of the gas from the initial value $T$ to the temperature which it acquires in the calorimeter. But the temperature of the latter changes from $T_1$ to $T_2$. Hence, the mean temperature of the gas in the calorimeter equals $(T_1 + T_2)/2$. The change in the temperature of the gas thus equals $T - (T_1 + T_2)/2$, and the heat it has given up is

$$Q = Mc_p\left(T - \frac{T_1 + T_2}{2}\right)$$

Therefore,

$$m(T_2 - T_1) = Mc_p\left(T - \frac{T_1 + T_2}{2}\right)$$

whence we get the following equation for the specific heat capacity:

$$c_p = \frac{m(T_2 - T_1)}{M\left(T - \frac{T_1 + T_2}{2}\right)} \tag{2.39}$$

and the molar heat capacity $C_p = \mu c_p$.

**Measurement of the Ratio $C_p/C_V$.** It has been shown on a previous page that the ratio of the heat capacities of gases $\gamma = C_p/C_V$ plays an important part in the theory of ideal gases because it determines the number of degrees of freedom of the molecules. In addition, this quantity is in the equation of an adiabat. It has still another part, namely, knowing the value of $\gamma$, we do not have to resort to measurements of $C_V$, which always involve considerable difficulties. We can obtain the value of $C_V$ from the measured values of $C_p$ and $\gamma$. This is exactly what experimenters often do.

There are several ways of measuring $C_p/C_V$. The way based on measuring the velocity of sound should be considered the most convenient and accurate of them. The matter is that the velocity of sound $u$ in a gas is determined by the formula

$$u = \sqrt{\gamma \frac{p}{\rho}}$$

where $p$ = pressure of the gas
$\rho$ = its density.

If $p$ and $\rho$ are known, then by measuring the velocity of sound $u$, we can calculate the value of $\gamma = C_p/C_V$. This method is convenient in that its use permits us to do without measuring the quantity of heat and the temperature. The ways of measuring the velocity of sound are described in other courses.

CHAPTER 3

# COLLISIONS OF MOLECULES AND TRANSPORT PHENOMENA

We have already noted that collisions between molecules play a very important part in all processes occurring in gases. Particularly, collisions are responsible for the setting in of equilibrium Maxwellian distribution of molecules by velocities. Collisions in general play a decisive part in the mechanism of the establishment of equilibrium in gases. We can even say that collisions are precisely the mechanism which ensures the transition of a gas to an equilibrium state and maintenance of such a state.

In the present chapter, we shall consider in greater detail collisions and their part in establishing equilibrium.

## 3.1. MOLECULAR MOTION AND TRANSPORT PHENOMENA

Calculation of the velocities of gas molecules using the basic equation of the kinetic theory

$$\frac{m\bar{v}^2}{2} = \frac{3}{2} kT$$

results in a very high numerical value of the velocity. At room temperature, it is found to equal (and this is confirmed by direct experiments) approximately 500 m/s for molecules of air and 1800 m/s for hydrogen molecules. These values seem to be unexpectedly high because at first sight they contradict some well-known facts.

Let us explain this with examples. In a state of equilibrium, the temperature of a gas in all the parts of the volume it occupies is the same. This means that the mean kinetic energy of the particles throughout the gas is identical. If we heat one part of the gas, equilibrium will be violated. But if we leave the gas alone after this, after a certain time equilibrium is restored — the temperature again becomes identical in all parts of the gas.

This levelling out of the temperature obviously occurs owing to the continuous movements of the molecules. The heated part of the gas contains more fast molecules than its other parts, but owing to molecular movements these fast molecules rush to where their number is smaller. Thus on an average their number becomes equal throughout the gas.

Naturally, molecules also move at the same time to the heated part so that the number of particles in a unit volume (and, consequently, the pressure) does not change either in the heated or in other parts of the gas. The only thing that happens is the transfer of energy from the part of the gas where there is more of it to the part where there is less. This process is called *heat* or *thermal conductivity*.

It should seem to follow from the fact that the velocities of molecules are very great that the temperature ought to level out very rapidly. Experiments show, however, that the thermal conductivity of gases is low. A considerable time elapses before the temperature of a gas levels out if one part of it is heated more than another.

Consider another example. Let us add to a gas filling a certain volume an admixture of another gas so that with an identical pressure and temperature throughout the entire volume the concentration of the admixture in one part becomes greater than in all the others. We see that after a certain time elapses the admixture is distributed throughout the entire volume, and the mixture of gases becomes homogeneous. Such levelling out of the concentrations which is obviously due to the motion of the admixture molecules in the direction of their smaller concentration is called *diffusion*. The place of the admixture molecules that changed their location is taken by other molecules so that the pressure of the gas here too remains constant. Only *transport of the mass* of the added gas occurs.

Since this transport is also ensured by motion of the molecules, and the velocities of the molecules are high, diffusion should seem to occur rapidly with the concentrations levelling out almost instantaneously. Experiments show, however, that at atmospheric pressure diffusion is a very slow process, and mixing in the absence of motion of the gas as a whole may last several days.

Finally, equilibrium of a gas may be violated by a flow velocity being imparted to one of its parts that differs from the flow velocity of the adjacent parts. Here too, owing to *momentum transport* from the rapidly moving to the slowly moving parts of the gas, the velocity of the entire gas after a certain time becomes identical in all its parts. This phenomenon is called *internal friction* or *viscosity*. And again, thermal motion of the gas particles is what is responsible for levelling out of the flow velocity of the gas. In this case too, equilibrium is restored more slowly, as shown experimentally, than could be expected with a view to the high velocities of molecular movements.

How can we explain that in all three examples given above the transport phenomena proceed slowly, although they are all due to rapid movements of the molecules?

The reason for this disparity is that in these phenomena of setting in of equilibrium an important part is played not only by the velocities of the molecules, but also by the *collisions* between them which evidently prevent the free movements of the molecules.

In view of the tremendous number of molecules typical of a gas at ordinary pressures, it is impossible to imagine that they could all find their path in the gas without interacting with one another so as to change their direction, i.e. without colliding with one another. The result of interaction between molecules is a collision between them.

Generally speaking, interaction between molecules may lead to the most diverse results. The molecules may deviate from their straight path (scatter), they may decompose into simpler parts (dissociate), for example into atoms, etc.

In this chapter, we shall be interested only in the process of a change in the direction of a molecule as a result of a collision. This process is often called the *scattering* of molecules.

A change in the direction of motion of molecules is caused by the forces of their interaction, which become appreciable only at small distances between them. This is why deviation of molecules from their initial direction occurs only when they get sufficiently close to one another. We will call the change in the direction of motion of a molecule through an *appreciable* angle under the action of another molecule a *collision* of the molecules.

It is precisely this concept of a collision that underlies the quantity used to characterize the geometrical dimensions of molecules. Here we use the concept of the dimensions of macroscopic bodies taken from our everyday experience. Imagine, for instance, the collision of two billiard balls. It always results in a change in the initial direction of motion of the balls. The radius of each of the balls equals half the distance between their centres upon mutual contact: the balls are exactly in this position at the moment of collision (Fig. 43). In the same way, we can determine the radius of a molecule as half the distance between its centre and that of another identical molecule which caused our molecule to deviate from the initial direction of its motion.

In other words, when dealing with collisions between molecules, we shall liken them to rigid elastic balls or spheres. This rough (and wittingly incorrect) approximation is justified by the fact that molecules in many respects do behave like rigid elastic spheres.

These "spheres" are actually complicated systems of charged particles, nuclei, and electrons between which forces of attraction and repulsion act that depend in a complicated way on the distance between the spheres (molecules). Although here we cannot speak of contact of the "surfaces"

of the molecules, nevertheless the dimensions of the molecules can be determined as the distance between their centres upon collision.

The question of the collisions of particles has a considerably greater significance in physics than the case of collisions between molecules we are considering. In many fields of physics, it becomes necessary to consider the interaction of particles with one another or of light quanta with particles

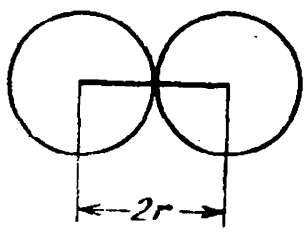



Fig. 43

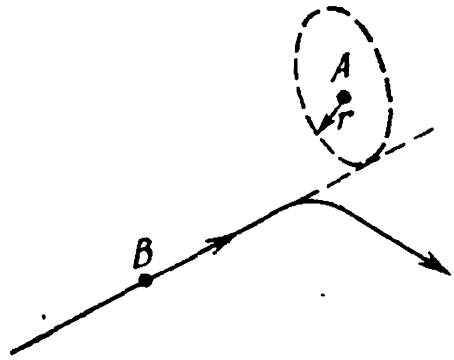



Fig. 44

of a substance, particularly with atomic nuclei. Such interaction may lead to the most diverse results and processes. Interaction may be followed, for example, by the elastic or inelastic scattering of a particle (or a quantum of light — a photon), its capture (a neutron in certain conditions may be captured by the nucleus it collided with forming a new artificial nucleus), and ionization of the atom.

In all these cases for a quantitative characteristic of a process, we introduce the concept of the *effective area of a cross section* or, for brief, the *cross section* of a given process. It is quite similar to the concept of the dimensions of molecules which we have introduced.

Imagine particle $B$ flying rectilinearly (Fig. 44). Assume further that for a process of interest to us to occur when this particle interacts with another particle $A$, it is necessary for particle $B$ to fly sufficiently close to particle $A$, for instance not farther than a certain distance $r$. If we draw around $A$ a circle with the radius $r$ whose plane is at right angles to the direction of motion of particle $B$, we can say that interaction of particles $A$ and $B$ will result in the process interesting us only if the target direction of particle $B$, i.e. a straight line coinciding with the direction of motion of its centre, passes inside the circle with the radius $r$.

It is the area of this circle $\sigma = \pi r^2$ that is called the cross section of a given process. Particularly, Fig. 44 shows a case when a collision resulted in deviation (scattering) of particle $B$ from its original direction of motion.

If we imagine the collision of molecules as that of rigid spheres, the radius of these molecules equals $r/2$ because upon the collision of two spheres the distance between their centres equals the double radius of the spheres (if the latter are identical). The cross-sectional area of such a sphere, i.e. the area of its great circle, equals $\pi r^2/4$. This means that the effective cross

section of molecules $\sigma$ is four times greater than the cross-sectional area of a molecule.

## 3.2. MEAN NUMBER OF COLLISIONS IN UNIT TIME AND MEAN FREE PATH OF MOLECULES

We shall as previously consider a gas to be ideal. In other words, we shall consider that, except for the moment of collision, molecules do not interact, are not subjected to the action of any forces, and therefore travel in a straight line. At the moment of collision, the direction of the velocity of a molecule changes, after which it again moves rectilinearly. The path of a molecule in a gas is thus a broken line similar, for example, to that shown in Fig. 45. Each deflection of the path notes a place of collision. The distance travelled by a molecule between two consecutive collisions is called the *free path.*

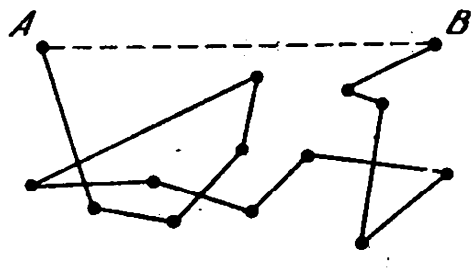


Fig. 45

Since the number of molecules in a gas is exceedingly great, we cannot speak of any regularity or order in the process of collisions, and the lengths of the straight sections along the zig-zag path of a molecule may be different. We shall therefore be interested in the *mean* free path. In exactly the same way, the *number of collisions* of a molecule in a unit time may be different. and we should speak only of the *mean* value of this quantity.

These two related quantities — the mean free path and the mean number of collisions in a unit time — are the main characteristics of the process of collisions of gas molecules. Particularly, the "hindrances" to the transport phenomena mentioned above depend on the number of collisions. This is what determines the length of the path of a molecule between two given points in a gas. A glance at Fig. 45 shows that the true path of a molecule between points $A$ and $B$ is much greater than beeline $AB$. For example, diffusion of a gas, i.e. the penetration of one gas into another, cannot proceed rapidly, notwithstanding the high velocity of the molecules: collisions to a considerable degree compensate for the influence of the velocity.

The mean number of collisions of a molecule of a gas in a unit time can be calculated on the basis of very simple considerations. We shall consider molecules to be rigid elastic spheres with a radius $r$. Assume that one of the molecules travels along a straight line in a gas where the particles are uniformly distributed throughout its volume so that each cubic centimetre contains $n$ molecules. Also assume first that all the molecules except one are at rest. Hence, our single moving molecule, travelling in one second a distance equal to its mean velocity $\overline{v}$, will collide with all the molecules in its path. These will be the molecules whose centres are within a cylinder

having a length of $\bar{v}$ and an area of its base equal to the effective cross section of collision (Fig. 46). The volume of this cylinder is $\sigma\bar{v}$, and the number of molecules in it is $\sigma\bar{v}n$. The number of collisions $Z$ of our molecule will be the same, i.e.

$$Z = \sigma\bar{v}n \tag{3.1}$$

It is quite natural that a molecule cannot travel along a straight line if it collides with other molecules. It actually travels along a zig-zag path as shown, for example, in Fig. 47. This does not change the results of our calculations, however. In assuming that a molecule travels along a straight line, we only mentally "straightened out" the broken cylinder shown in Fig. 47.

It should be taken into account that not one, but all the molecules of a gas travel. This means that the expression for $Z$ should include not the

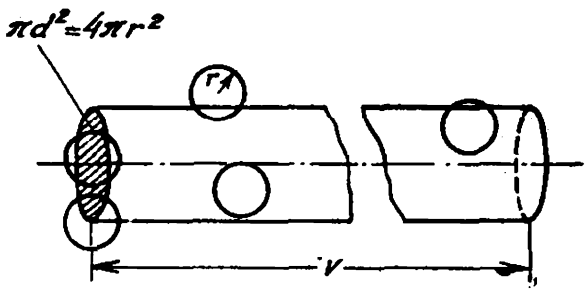



Fig. 46

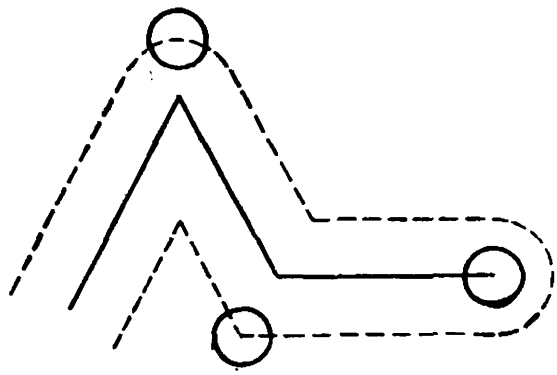


Fig. 47

absolute (relative to the walls of the vessel) velocity of a molecule, but its velocity $v_{rel}$ relative to the molecules which it collides with. We can show, taking into account the Maxwellian velocity distribution of molecules, that the relative velocity $v_{rel}$ is related to the absolute velocity $\bar{v}$ as follows:

$$v_{rel} = \sqrt{2}\,\bar{v}$$

Hence for the mean number of collisions of a molecule in a unit time, we get the equation

$$Z = \sqrt{2}\sigma\bar{v}n \tag{3.2}$$

or, since we have agreed to considering the molecules as spheres,

$$Z = 4\sqrt{2}\pi r^2\bar{v}n \tag{3.3}$$

To find the mean number of collisions in a unit time in a gas, i.e. the collisions of all the molecules, we must multiply $Z$ by the number of molecules $N$ in the gas. But since two molecules participate in each collision (the probability of three or more molecules colliding simultaneously is very low), this number also has to be divided by two so as not to count each

collision twice. Hence, the total number of collisions in a gas containing $N$ particles is

$$Z' = \frac{NZ}{2} = 2\sqrt{2}\,\pi r^2 \bar{v} n N$$

Thus, the number of collisions occurring every second in a *unit volume* of a gas is

$$Z'' = \frac{nZ}{2} = 2\sqrt{2}\,\pi r^2 \bar{v} n^2$$

where $n$ is the number of molecules in a unit volume.

Knowing the number of collisions of one molecule in a unit time, we can easily calculate the mean free path.

During the time $t$, a molecule travels a certain zig-zag path equal to $\bar{v}t$. The number of deflections along this path equals the number of collisions because each deflection is the result of a collision. The mean free path, i.e. the mean length of the straight section $l$ between collisions, equals the ratio of the length of the path travelled by a molecule to the number of collisions it participated in along this path:

$$l = \frac{\bar{v}t}{Zt} = \frac{\bar{v}}{Z}$$

or, substituting for $Z$ its value from Eq. (3.3), we get

$$l = \frac{1}{4\sqrt{2}\,\pi r^2 n} = \frac{0.057}{r^2 n} \tag{3.4}$$

This equation allows us to find the numerical values of $Z$ and $l$. Let us perform such calculations for air (nitrogen) in standard conditions (a pressure of 1 atm and a temperature of 273 K). The radius $r$ of a nitrogen molecule can be taken equal to $1.9 \times 10^{-10}$ m, the number of particles in a unit volume $n = 2.7 \times 10^{25}$ m$^{-3}$, and the mean velocity $\bar{v} \approx 5 \times 10^2$ m/s. Hence,

$$Z = 4\sqrt{2} \times 3.14 \times (1.9 \times 10^{-10})^2 \times 5 \times 10^2 \times 2.7 \times 10^{25} \approx$$

$$\approx 8.6 \times 10^9 \text{ s}^{-1}$$

The mean free path of a molecule in these conditions is

$$l = \frac{\bar{v}}{Z} \approx 0.6 \times 10^{-7} \text{ m}$$

The question naturally appears whether we may consider a gas to be ideal whose particles collide thousands of millions of times a second and travel insignificant distances not exceeding a few ten-thousandths of a centimetre between collisions, i.e. "freely". May we consider that molecules of such a gas do not interact? A collision is *interaction* resulting in a change

in the direction of the velocity of molecules, and such frequent collisions would seem to point to very great interaction. It is easy to see, however, that matters are different. Indeed, as indicated above, molecules interact with one another only during the time the distance between them is of the order of magnitude of their diameter $d$, i.e. $10^{-10}$ m. The remaining time between collisions, the molecules travel freely. Since at atmospheric pressure the free path of a molecule $l$ is of the order of magnitude of $10^{-7}$ m, which is about 1000 times greater than the dimensions of a molecule, the duration of its free travel is the same number of times $(l/d)$ greater than the time spent by the molecule in mutual interaction.

In other words, the duration of collisions of molecules is about one-thousandth of the time between collisions. Hence, molecules spend the overwhelming part of their time in free motion, and collisions, even at atmospheric pressure, may be considered as a rare event in their life.

**Dependence of Free Path on Pressure.** Inspection of Eq. (3.4) shows that the free path of molecules is inversely proportional to their number in a unit volume and, therefore, to the pressure $p$ so that we can write

$$l \propto \frac{1}{p}$$

Diminishing of the pressure is attended by a corresponding increase in the free path of a molecule. At a definite pressure, the free path becomes equal to the dimensions of the vessel containing the gas, and exceeds them upon a subsequent drop in the pressure. For instance in a vessel having a diameter of about 25 cm (a size usual in laboratory practice), the free path of a molecule becomes equal to the diameter of the vessel already at a pressure of about $10^{-7}$ atm ($7 \times 10^{-5}$ mm Hg). It is comparatively simple to create such a pressure because modern pumping means make it possible to obtain a pressure as low as from $10^{-11}$ to $10^{-12}$ mm Hg.

When the free path becomes equal to or greater than the dimensions of the vessel, virtually no collisions of the molecules occur in a gas, and the molecules travel the whole distance from one wall to another in a straight line.

We can expect a gas whose molecules do not collide with one another to differ in its properties from an ordinary gas. We shall acquaint ourselves with the distinctive features of such a gas in Chap. 4.

**Dependence of Free Path on Temperature.** It follows from Eq. (3.4) that the free path of molecules should not depend on the temperature. Experiments show, however, that there is such a relationship, although only a slight one. Elevation of the temperature is attended by a growth in the free path. The explanation is that by Eq. (3.4) the free path $l$ is inversely proportional to the cross section of a molecule. The latter quantity, as we know, is determined by the distance remaining between the molecules when they collide, i.e. by the distance at which the force of interaction

between the molecules already causes an appreciable change in their direction.

It is easy to see that the cross section of molecules should depend on their velocity (energy) because at the same force of interaction the rapid molecules deviate less from their path than the slower ones. Consequently, the higher the velocity of molecules, the greater must be the force causing them to deviate and, therefore, the smaller must be the distance between them upon collision. Thus, the cross section of molecules diminishes with an increase in their velocity, i.e. with elevation of the temperature of the gas. The free path of molecules, however, grows with increasing temperature. This slight dependence of $l$ on the temperature explains certain phenomena that will be treated below.

The temperature dependence of the free path can confirm the considerations set out above on the meaning of the concept "dimension of a molecule". If molecules were indeed rigid spheres, a change in their dimensions upon a change in velocity would be out of the question. Actually, the dimensions of particles (not only of gas molecules!) are determined by the distance of closest approach. The latter cannot fail to depend on the velocity of the particles and, consequently, on the temperature (for gas molecules). This, however, is not a hindrance to considering the interaction between molecules in a number of cases as interaction between rigid spheres without considerably detracting from accuracy.

## 3.3. EFFECTIVE CROSS SECTION OF A PARTICLE AND PROBABILITY

It is easy to give a meaning other than geometrical to the effective cross section of a molecule (or of any other particle).

Imagine a layer of a gas having a thickness of $\Delta x$ and a cross-sectional area of 1 cm$^2$. Assume that the gas consists of molecules having a section $\sigma$ and a density (their number in a unit volume) equal to $n$. Assume, as we have done before, that all the molecules of the layer are at rest, and a single molecule approaches it. When the latter passes through the layer, it may collide with the molecules in it. This molecule, naturally, is not "aimed" at any of the molecules in the layer so that its collision with one of them is a matter of chance. The total area of the sections of all the molecules in the layer is

$$\Delta A = \sigma n \Delta x \times 1 \text{ cm}^2$$

If the gas is so rarefied that the projections of the sections of the molecules do not overlap, the molecule flying toward the layer will "see" ahead of it an area of 1 cm$^2$, a portion of which equal to $\sigma n \Delta x$ is occupied by molecules. If this area equalled 1 cm$^2$, i.e. covered the entire area of the layer, our molecule would not be able to avoid colliding with a molecule in the layer. We can say that in this case the *probability of a collision* would equal

unity. In general, a molecule has the more chances of a collision, the greater is the fraction of the area of the layer formed by the total area of the cross sections of all its molecules.

The following mechanical analogue will help us to understand the molecular situation being considered. Imagine a portion of a fence made of pickets or stakes with free spaces between them. Not far from the fence, a child who has accumulated a large stock of pebbles (and patience!) is throwing them (naturally without aiming) in the direction of the fence so that the pebbles are approximately uniformly distributed over the portion of the fence under consideration. Evidently, some of the pebbles thrown by the child will pass through the spaces between the stakes, and the others will hit the stakes. After using up his stock of pebbles (if it was big enough), the child could see that the ratio of the number of pebbles that passed through the fence to the total number of pebbles thrown at it is approximately equal to the ratio of the spaces in the selected portion of the fence to its total area. The first of these ratios is that of the number of trials favouring an event (the passing of a pebble through the fence) to the total number of trials. According to our definition, it equals the probability of the event. Hence, the ratio of the area of the spaces to the total area of the fence equals this probability.

Returning to the flying molecule encountering the layer of a gas, we can say here too that every molecule flying toward the layer may collide with a molecule in it, but may also pass through it without any collision. If such an experiment is repeated a sufficiently great number of times, however, the ratio of the number of collisions to the total number of experiments will obviously equal the ratio of the area of the cross sections of all the molecules in the layer to the area of the layer (1 $cm^2$ in our example).

Thus, the quantity $\sigma n \Delta x$ which is exactly equal to this ratio is the probability of a molecule colliding with another one along the path $\Delta x$ in a gas. The probability of a collision along a path of 1 cm is evidently equal to $\sigma n$, i.e. to the product of the area of the effective cross section of the molecules and the number of molecules in a unit volume. If the thickness of the layer were equal to the free path, the molecule would collide with another one without fail. This would mean that the total "visible" area of the cross sections of all the molecules in such a layer would equal the area of the layer, i.e. 1 $cm^2$:

$$\sigma n l \times 1 = 1 \text{ cm}^2$$

The effective cross section of the molecules $\sigma$ is therefore related to the *probability of a collision* (scattering) between molecules and does not have a purely geometrical meaning. If the effective cross section is great, this does not mean that we are dealing with a "big" molecule, but only means that the probability of a collision is great. This explains why the effective cross section may be different even for the same particles in different conditions and for different processes. We would not be able to understand

this if the effective cross section were indeed simply the geometrical area of the cross section of a molecule considered as a rigid sphere.

The probability meaning of the effective cross section of a molecule will become especially clear if we use the expression obtained earlier for the mean number of collisions in a unit time:

$$Z = \sigma \bar{v} n$$

[see Eq. (3.1)]. It follows from this equation that the quantity $\sigma n$ equal to $Z/\bar{v}$ is the number of collisions $z'$ along a path of 1 cm:

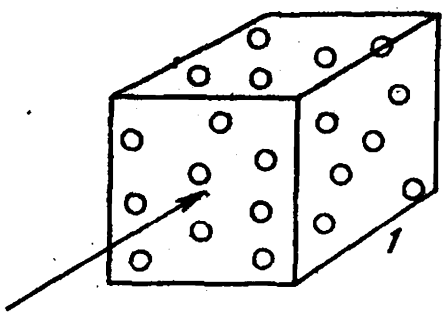



Fig. 48

$$\sigma n = \frac{Z}{\bar{v}} = z'$$

whence

$$\sigma = \frac{z'}{n} \tag{3.5}$$

It follows from Eq. (3.5) that the quantity $\sigma$ should be given a probability meaning. Again imagine a layer of a gas, this time 1 cm thick and having an area of 1 cm$^2$ (Fig. 48) which a moving molecule is approaching. It may collide with any of the $n$ molecules in our layer (whose volume is 1 cm$^3$). Actually, however, $z'$ collisions occur instead of $n$. Hence, the ratio $z'/n$ in Eq. (3.5) is the ratio of the number of events (collisions) that have occurred to the number of possible ones, and the latter, as we know, equals the probability of the event being considered (see Sec. 1.10).

The circumstance that a probability meaning is attributed to the effective cross section of a molecule or another particle is no hindrance to its being measured in units of area. Particularly, it is not difficult to see that the quantity $z'/n$ has the dimension of area.

In physics, a special unit has been introduced for the effective cross section and is connected with the dimensions of an atomic nucleus. It is called the *barn* and equals $1 \times 10^{-24}$ cm$^2$.

## 3.4. SCATTERING OF A MOLECULAR BEAM IN A GAS

The attenuation of a molecular beam passing through a gas is connected with collisions of the molecules in the gas.

Assume that a certain number of molecules (a molecular beam) having a definite velocity, whose magnitude and direction are the same for all the molecules, are passing through a gas. Owing to the collisions with the molecules of the gas, part of the molecules of the beam will change the direction of their motion (scatter) and leave the beam. The number of such molecules leaving the beam will grow as it passes through the gas, leaving fewer and fewer particles in the beam. The latter will melt, as it were, losing its particles.

Suppose that the beam is travelling in the gas along the $X$-axis, and at the beginning of its path at $x = 0$ the number of particles in it is $N_0$. After the beam covers the path $dx$, the number of particles in it will lower by $dN$ and become equal to $N$. The ratio of the number of particles that have "quitted the ranks" to the remaining number equals the ratio of the path $dx$ travelled by the beam to the free path $l$ because the greater this ratio (i.e. the greater the number of free paths contained in the length $dx$), the more are the chances of each molecule to be deviated upon a collision. Therefore

$$-\frac{dN}{N} = \frac{dx}{l}$$

The minus sign indicates that the number of particles in the beam diminishes ($dN < 0$). This equation can also be written as follows:

$$d \ln N = -\frac{dx}{l}$$

Integration of this equation yields

$$\ln N = -\frac{x}{l} + C$$

where $C$ is an integration constant. It can be found from the condition that when $x = 0$ the number of particles $N = N_0$. Hence, $C = \ln N_0$, and

$$\frac{N}{N_0} = e^{-x/l} \quad \text{or} \quad N = N_0 e^{-x/l} \tag{3.6}$$

This equation shows the law followed by attenuation of a beam in a gas: the number of particles in a beam diminishes according to an exponential law with a growth in the thickness $x$ of the layer of the gas being penetrated.

The quantity $1/l$ (the reciprocal of the free path) determining the steepness of the exponential curve is called the *scattering factor*. A glance at Eq. (3.6) shows that if there are no collisions in a gas (formally this corresponds to $l = \infty$), there is no scattering — the beam does not change its density, and $N$ remains equal to $N_0$ at any values of $x$.

It should be noted that by using Eq. (3.6), we can get an expression for $l$ coinciding with Eq. (3.4). For this purpose, we must find the mean value of $l$ for all the velocities of the molecules with account taken of the Maxwellian distribution.

## 3.5. EXPERIMENTAL DETERMINATION OF THE FREE PATH

Measurement of the free path of particles is very important because the quantity $l$ is connected with the effective dimensions of molecules and, therefore, with the forces of their interaction.

We shall describe here a method for the direct measurement of the free path of particles in a gas in which the method of the molecular beam that we have already been acquainted with is used (M. Born and E. Borman, 1920).

The apparatus is shown schematically in Fig. 49. From heat source $H$, the stream of evaporated silver atoms passes through narrow diaphragm $D$ and leaves it upward in the form of a sharply outlined beam of atoms. Four plates $P_1$, $P_2$, $P_3$, and $P_4$ are spaced at 1 cm along the path of the beam. Round holes are cut out in all four plates, and the beam of silver atoms flies toward them. But a glass quadrant whose apex coincides with the centre of the hole is attached to each plate (shown separately in Fig. 49). The quadrants are turned relative to one another through an angle of 90 degrees so that all together they completely close the channel formed in the plates.

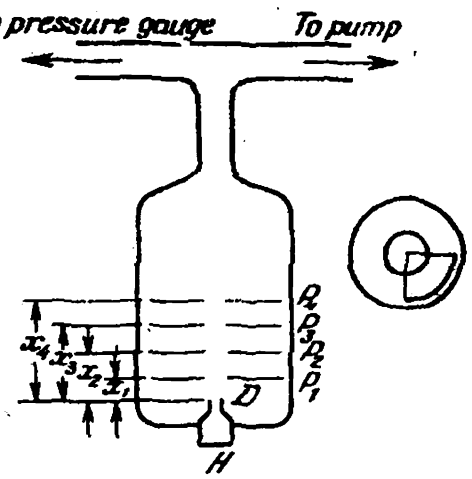


Fig. 49

When the beam passes through the holes, one-fourth of all the atoms from the beam are deposited on each of the quadrants (a deposit is formed only at the apices of the quadrants closing the holes). Since the plates are at different distances from source $H$, the density of the deposit on them will be different. The farther a plate is, the smaller is the density of the deposit.

The plates with the quadrants and the source of atoms are placed in a quartz tube in which different pressures of the air can be created with the aid of a pump. The plates are cooled with liquid nitrogen.

The experiment consists in evaporation of the silver and subsequent measurement of the relative density of the deposits on the quadrants, which is proportional to the number of particles reaching them. Letting $D_1$, $D_2$, $D_3$, and $D_4$ stand for the densities of the deposits on the quadrants at a given pressure of the gas, for any pair of quadrants we can write Eq. (3.6). For instance for the first and second quadrants, we get

$$D_1 = D_0 e^{-x_1/l} \quad \text{and} \quad D_2 = D_0 e^{-x_2/l} \tag{3.7}$$

where $D_0$ = density of the deposit at the minimum pressure when the free path is equal to or greater than the dimensions of the vessel and there is no scattering

$x_1$ and $x_2$ = distances to the plates from source $H$.

With good running of the experiment, the density of the deposit $D_0$ should be the same on all the quadrants. This was confirmed by the relevant measurements.

It is simple to calculate $l$ from the two equations (3.7):

$$l = \frac{x_2 - x_1}{\ln\left(\frac{D_1}{D_2}\right)} \tag{3.8}$$

Since in the experiments run by Born and Borman the plates were spaced at 1 cm, i.e. $x_2 - x_1 = 1$, then

$$l = \frac{1}{\ln\left(\frac{D_1}{D_2}\right)}$$

The experiments showed that the values of $l$ satisfactorily agree with the above theory. It was also shown that in accordance with the theory the product of the free path and the pressure of a gas $lp$ remains the same at different pressures.

The measured values of the free path $l$ can also be used to calculate the dimensions of molecules. It must be noted, however, that the main quantitative data for the free paths of gas molecules and, consequently, for their cross sections were obtained not by the direct measurement of $l$ using the method described above, but from investigations of transport phenomena — diffusion, thermal conductivity, and viscosity. As we have indicated in Sec. 3.1, the phenomena of levelling out of the concentration, temperature or velocities of separate portions of a gas are determined by collisions between the molecules during their thermal motion. It is therefore clear that investigation of transfer phenomena should provide the possibility of determining the basic quantity characterizing collisions — the free path and, therefore, the cross section of the molecules. We shall now go on to a consideration of these phenomena.

## 3.6. DIFFUSION IN GASES

The phenomenon of the penetration of two or more contacting substances into one another is called diffusion. Diffusion appears in a gas (as in any other substance) if it is not homogeneous in composition, i.e. if it consists of two or more different components whose concentration changes from point to point. Diffusion consists in the passing of each of the components of a mixture from the parts of the volume of a gas where its concentration is greater to where it is smaller, i.e. in the *direction of a drop in concentration.*

The motion of a component under the action of a concentration gradient is called the *diffusion flux* of this component. It is measured by the quantity of diffusing component that passes in a unit time through a unit area at right angles to the direction of diffusion, i.e. to the direction of the drop in concentration.

The diffusion flux can be expressed in units of mass. Hence, in the SI system it is measured in $kg/m^2 \cdot s$ and in the cgs system in $g/cm^2 \cdot s$. It can also be expressed by the number of moles ($mol/cm^2 \cdot s$) or molecules ($molecule/cm^2 \cdot s$), etc. The same relates to the concentration of a given component, which may be expressed in $kg/m^3$, $g/cm^3$, $mol/cm^3$, etc.

The diffusion flux caused by a concentration gradient results in levelling out of the concentrations, i.e. in diminishing of the concentration gradient that caused this flux. A heterogeneous gas mixture left to itself with time becomes homogeneous owing to diffusion (the gases mix).

Any process in which the parameters of the system participating in it change with time is called a *non-stationary* process unlike a *stationary* process when the quantities characterizing the system do not change with time. Diffusion resulting in levelling out of the concentrations, i.e. in a change in the concentration gradients and in the concentrations of the components themselves, is called *non-stationary* or *unsteady-state diffusion*. We can also imagine *steady-state diffusion* when the concentrations of the components of a mixture are kept constant in some artificial way. For this purpose, the given component must be continuously added to one part of a vessel and removed in the same amount from another part of it. Most often, we have to do with unsteady-state diffusion.

**The Basic Law of Diffusion (Fick's Law).** It has been proved experimentally that the diffusion flux of a component is proportional to the concentration gradient of this component taken with the reverse sign (Fick's law).

We shall remind our reader here that by a gradient of a quantity (scalar) $G$ depending on coordinates is meant the vector characterizing the rate of change of this quantity in space. The vector is arranged in the direction of the most rapid growth in $G$ and is numerically equal to the rate of this growth.

In the following, we shall be interested in quantities changing along a single direction, for example along the $X$-axis. Here the numerical value of the gradient of $G$ (its symbol is grad $G$) equals the rate of change in the quantity $G$ with a change in $x$, i.e. the derivative $\partial G/\partial x$. And since we assumed that the quantity $G$ changes only along the $X$-axis, we can substitute the total derivative $dG/dx$ for the partial one $\partial G/\partial x$. Thus,

$$\text{grad } G = \frac{dG}{dx}$$

i.e. the change in the quantity $G$ per unit length.

If the concentration $w$ of the component of the gas mixture of interest to us changes along the $X$-axis (and does not change in other directions), the quantity

$$\text{grad } w = \frac{dw}{dx}$$

is called the *gradient of the concentration w*.

Consequently, the basic law of diffusion (Fick's law) is

$$I = -D\frac{dw}{dx} \tag{3.9}$$

where $I$ is the diffusion flux of the component we are interested in along the $X$-axis. The minus sign in the right-hand side of Eq. (3.9) shows that the diffusion flux is directed toward diminishing of the concentration. The factor $D$ in Eq. (3.9) is called the *diffusion coefficient*. It numerically equals the diffusion flux at a gradient of concentration equal to unity.

Let us find the units of the diffusion coefficient in the SI and cgs systems. From Eq. (3.9), we have $D = \frac{I}{dw/dx}$. The diffusion flux $I$ is measured in kg/m$^2$·s (SI) or g/cm$^2$·s (cgs). The concentration $w$ is measured in kg/m$^3$ (SI) or g/cm$^3$ (cgs); hence, the gradient of concentration $dw/dx$ is measured in kg/m$^4$ (SI) or g/cm$^4$ (cgs). It follows that the diffusion coefficient $D$ is measured in m$^2$/s (SI) or cm$^2$/s (cgs).

The amount of substance in Eq. (3.9) must naturally be expressed in both sides of the equation in the same units. This means that if the flux of the diffusing component is expressed by its mass $M$ (number of grammes) flowing through 1 cm$^2$ in a unit time, then the concentration $w$ must be expressed by the number of grammes of the given component in 1 cm$^3$ of the mixture. The concentration $w$ in this case is the partial density of the component, $w = \rho$. Equation (3.9) now becomes

$$M = -D\frac{d\rho}{dx} \tag{3.10}$$

If the flux of the diffusing component is expressed by the number of particles $N$ flowing through 1 cm$^2$ in one second instead of by the mass, then the concentration must be expressed by the number of particles in one cubic centimetre, and Eq. (3.9) becomes

$$N = -D\frac{dn}{dx} \tag{3.11}$$

The diffusion coefficient $D$ depends on the properties of the diffusing substance and of the remaining components forming the mixture (in the following we shall assume that there are altogether two components). At not too great concentrations of an admixture, however, it depends on the concentration itself to a very small extent.

In steady-state diffusion, the gradient of the concentration remains constant in time. The diffusion flux, therefore, also remains constant. In unsteady-state diffusion, the gradient of the concentration changes (the concentration levels out). The diffusion flux changes with time accordingly.

## 3.7. UNSTEADY-STATE DIFFUSION

Let us consider unsteady-state diffusion, i.e. a process of levelling out of the concentrations, in the following very simple case which, though being difficult to carry out in practice, gives a clear idea of the mechanism of the process.

Suppose that two vessels having the volumes $V_1$ and $V_2$ are connected to each other by a tube with the length $l$ and cross-sectional area $A$ (Fig. 50).

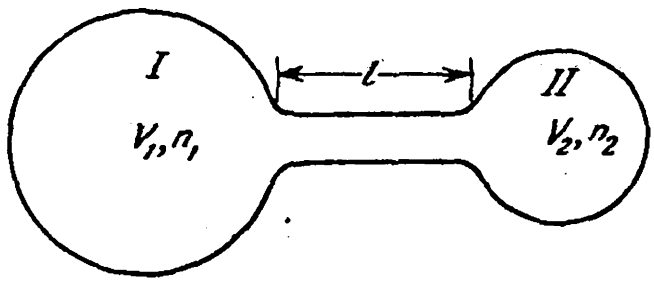



Fig. 50

They are filled with a mixture of gases having different compositions but with identical temperatures and pressures. Assume that the concentrations of the component we are interested in are $n_1$ and $n_2$ in the two vessels, respectively, and that $n_1 > n_2$.

Owing to diffusion, the concentrations in both vessels will level out, i.e. the difference in concentrations $\Delta n = n_1 - n_2$ will diminish with time. Let us determine the law according to which this diminishing of the concentration occurs. It follows from Fick's law that the diffusion flux

$$I = -D\frac{dn}{dx}$$

To simplify our reasoning, we shall assume that the concentration of the component being considered is low. Hence, we may assume that

$$\frac{dn}{dx} = \frac{\Delta n}{l}$$

and Eq. (3.11) becomes

$$N = -D\frac{\Delta n}{l}$$

Upon diffusion, molecules of the diffusing component will pass from vessel *I* to vessel *II*. The number of molecules diffusing into vessel *II* during the infinitely small interval of time $dt$ is

$$dN = D\frac{\Delta n}{l}A\,dt \qquad (3.12)$$

(it should be remembered that with respect to its absolute value the diffusion flux, in the given case $D\frac{\Delta n}{l}$, is the number of molecules passing in a unit time through a unit area). Owing to this transition of the molecules, their density in vessel *I* diminishes by a certain amount $dn'$, and in vessel *II* grows by $dn''$. It is obvious that

$$dn' = -\frac{dN}{V_1} \quad \text{and} \quad dn'' = \frac{dN}{V_2}$$

Therefore, the concentrations $n_1'$ and $n_2'$ of the molecules in vessels *I* and *II* after the time *dt* elapses will become different:

$$n_1' = n_1 + dn' = n_1 - \frac{dN}{V_1} \quad \text{and} \quad n_2' = n_2 + dn'' = n_2 + \frac{dN}{V_2}$$

Consequently, their difference after this time will be

$$\Delta n' = n_1' - n_2' = n_1 - n_2 - \left(\frac{1}{V_1} + \frac{1}{V_2}\right) dN$$

Using here the value of $dN$ from Eq. (3.12) and assuming that $n_1 - n_2 = \Delta n$, we get

$$\Delta n' = \Delta n - D\frac{\Delta n}{l}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) A\, dt$$

Hence it follows that the change in the difference of the concentrations during the time *dt* is

$$d(\Delta n) = \Delta n' - \Delta n = -D\,\Delta n\,\frac{V_1 + V_2}{V_1 V_2}\,\frac{A}{l}\,dt$$

The quantity $V_1V_2/(V_1 + V_2) = V_0$ is called the *reduced volume* (when $V_1 = V_2 = V$, the reduced volume $V_0 = V/2$). Consequently,

$$d(\Delta n) = -D\,\Delta n\,\frac{1}{V_0}\,\frac{A}{l}\,dt$$

or

$$\frac{d(\Delta n)}{\Delta n} = -D\,\frac{A}{V_0 l}\,dt \tag{3.13}$$

Integration of Eq. (3.13) yields:

$$\ln \Delta n = -D\,\frac{A}{V_0 l}\,t + \ln C \tag{3.14}$$

where $C$ is an integration constant. Hence,

$$\Delta n = C \exp\left(-D \frac{A}{V_0 l} t\right) \tag{3.15}$$

The constant $C$ is easy to find if we know the initial difference of concentrations $\Delta n_0$, i.e. the difference at the moment $t = 0$. Indeed, introducing $t = 0$ and $\Delta n = \Delta n_0$ into Eq. (3.15), we get

$$C = \Delta n_0$$

whence

$$\Delta n = \Delta n_0 \exp\left(-D \frac{A}{V_0 l} t\right) \tag{3.16}$$

This equation is what answers our question about the law showing how the concentration difference diminishes with time. We see that the concentration difference diminishes with time according to an exponential law, and at a higher rate, the greater is the value of the quantity $D \frac{A}{V_0 l}$. The latter is constant for a given experiment. It should be noted that the reciprocal of this quantity

$$\tau = \frac{1}{D} \frac{V_0 l}{A} \tag{3.17}$$

has the dimension of time. It is easy to understand its physical meaning from Eq. (3.16). It follows from the latter that when $t = \tau$ the difference in concentrations $\Delta n$ becomes equal to $\Delta n_0/e$, i.e. it is $1/e$ of the initial value. Thus, the meaning of the constant $\tau$ consists in that it equals the interval of time needed for the concentration of the diffusing component to become $1/e$ of its previous value. The constant $\tau$ is generally called the *time constant of a process*.

Equation (3.16) can now be rewritten in the form

$$\Delta n = \Delta n_0 \exp\left(-\frac{t}{\tau}\right) \tag{3.18}$$

Physicists often have to do with equations containing a time constant in some form or other, like Eq. (3.18), in considering a process in which some of the parameters level out in an isolated system. From this standpoint, any similar process can be considered as a sort of diffusion. It is clear that the smaller the time constant, the more rapidly does the process of levelling out occur.

Diffusion in gases at atmospheric pressure, generally speaking, is a slow process. To obtain a quantitative idea of how slowly the concentrations level out, let us perform numerical calculations for the schematic experiment we have considered.

Assume that the vessels shown in Fig. 50 have equal volumes, $V_1 = V_2 = 1\ \text{dm}^3 = 10^{-3}\ \text{m}^3$. Assume further that vessel *I* is filled with a mixture of nitrogen and oxygen while vessel *II* contains pure nitrogen. If the length of the connecting tube $l = 10\ \text{cm} = 0.1\ \text{m}$ and its cross-sectional area $A = 1\ \text{cm}^2 = 10^{-4}\ \text{m}^2$, then taking from Table 7 (p. 156) the value of the diffusion coefficient for oxygen in nitrogen equal to $1.74 \times 10^{-5}\ \text{m}^2/\text{s}$ (at atmospheric pressure), we find that the time constant for our experiment is

$$\tau = \frac{1}{D}\frac{V_0 l}{A} = \frac{1}{1.74 \times 10^{-5}}\frac{10^{-3} \times 10^{-1}}{10^{-4}} = 5.75 \times 10^4\ \text{s} \approx 16\ \text{h}$$

This means that in about 16 hours the difference between the concentrations will diminish by less than three times.

### 3.8. STEADY-STATE DIFFUSION: CALCULATION OF THE DIFFUSION COEFFICIENT

We have already mentioned that the kinetic theory of gases permits us to explain the slow rate of diffusion quite simply, notwithstanding the high values of the velocities in the thermal motion of molecules. The reason is that for a molecule of a gas to get from one point to another, collisions make it travel along a long zig-zag path that is many times greater than a beeline between the points.

In addition to such a qualitative explanation, the kinetic theory also allows us to quantitatively assess the value of the diffusion coefficient and express it through molecular quantities — the free path of molecules and the velocities of their thermal movements.

Consider area *A* in a vessel containing a gas mixture (Fig. 51). The area is perpendicular to the *X*-axis, along which a constant difference of concentrations $\Delta n = n_1 - n_2$ is maintained (consequently, we are dealing with a steady-state process). To do away with ambiguity, assume that $n_1 > n_2$. Owing to thermal motion, the molecules of the component we are interested in will travel through area *A* both from left to right and from right to left. The difference between the concentrations at both sides of the area gives birth to a diffusion flux along the *X*-axis. It is equal to the difference between the number of molecules $N_1$ intersecting $1\ \text{cm}^2$ of area *A* per second (at right angles to its plane) in the direction of positive values of *X* (to the right) and the number of molecules $N_2$ intersecting the same section and during the same time in the opposite direction (to the left):

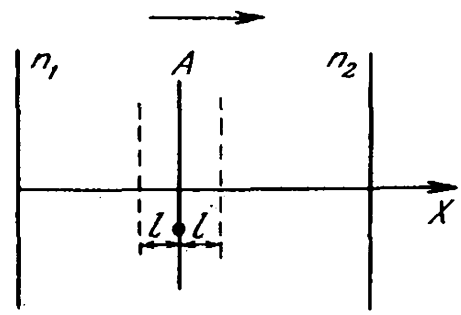


Fig. 51

$$N = N_1 - N_2$$

How can we determine the number of molecules intersecting 1 cm² of the area? If all the molecules travelled with the same velocity $v$ directed along the $X$-axis, the number of molecules intersecting an area of 1 cm² in one second would be $nv$, where $n$ is the number of molecules in a unit volume.

Actually, the molecules are distributed by velocities, but for a rough assessment we shall assume that all the molecules have the same velocity equal to the mean value $\bar{v}$. We shall also assume that the thermal velocities of the molecules are uniformly distributed along three mutually perpendicular directions. Consequently, of all the molecules in a unit volume, one-third travel along the $X$-axis, and half of these travel in the positive direction of this axis, i.e. toward area $A$, whereas the other half travel in the opposite direction, away from it.

Hence, the number of molecules $N_1$ intersecting 1 cm² of area $A$ in one second from left to right, and the number of molecules $N_2$ intersecting the same area in the opposite direction will be expressed by the equations

$$N_1 = \frac{1}{6} n' \bar{v} \quad \text{and} \quad N_2 = \frac{1}{6} n'' \bar{v}$$

Here $n'$ and $n''$ are the concentrations of the molecules at the two sides of the area. It must be noted with regard to the values of the quantities $n'$ and $n''$ that they vary along the $X$-axis owing to the molecules colliding with one another. Therefore, the molecules approach the area we have chosen having the values of the concentrations $n'$ and $n''$ which were created upon the last collision before the area. We must thus consider that $n'$ and $n''$ are the numbers of molecules in a unit volume that were at the distance $l$ (the mean free path) from the area at both sides of it.

The diffusion flux $N$ is therefore determined by the expression

$$N = N_1 - N_2 = \frac{1}{6} (n' - n'') \bar{v}$$

where $n' - n''$ is the difference between the concentrations at points at a distance of $2l$ from each other. It is not difficult to determine this difference if we know the value of the concentration gradient $dn/dx$ (we shall assume that $n$ changes only along the $X$-axis; i.e. we can write $dn/dx$ instead of $\partial n/\partial x$). Since $dn/dx$ is the difference in concentrations per unit length, for the distance $2l$ we have

$$n' - n'' = -2l \frac{dn}{dx}$$

This equation holds if $l$ is sufficiently small.

Thus, for a diffusion flux, we get the equation

$$N = -\frac{1}{3} l \bar{v} \frac{dn}{dx}$$

or, after multiplying both sides of this equation by the mass of a molecule $m$, we have

$$M = -\frac{1}{3} l\bar{v} \frac{d\rho}{dx}$$

By comparing the latter equation with Eqs. (3.11) and (3.10) of Fick's law, i.e.

$$N = -D\frac{dn}{dx} \quad \text{and} \quad M = -D\frac{d\rho}{dx}$$

we find the expression for the diffusion coefficient we are interested in:

$$D = \frac{1}{3} l\bar{v} \tag{3.19}$$

Inspection of Eq. (3.19) shows that the diffusion coefficient is inversely proportional to the pressure of a gas (because $l$ is proportional to $1/p$) and directly proportional to the square root of the temperature ($\bar{v}$ is proportional to $\sqrt{T}$).

In deriving Eq. (3.19), no account was taken of diffusion of the second component, which also takes place. And it cannot fail to affect the diffusion of the mixture component being considered.

For instance in a mixture of hydrogen and carbon dioxide, the hydrogen should diffuse at a considerably higher rate than the carbon dioxide because at any given temperature the mean velocity of the thermal movements of hydrogen molecules is almost five times greater than that of carbon dioxide, and the free path of the hydrogen molecules is also greater. But this means that the volume of the hydrogen transported in one direction is greater than the volume of the carbon dioxide transported in the opposite one. In this case, a pressure difference inevitably appears in the gas and, consequently, a flow of the gas as a whole. We defined diffusion, however, as a process in which the pressure of the gas mixture at all points remains constant, and the gas as a whole is at rest. But in an actual process of mutual diffusion of two different gases into one another, the higher value of the diffusion flux of one of them in comparison with the other is balanced by the flowing of the entire gas in the direction of the region where the molecules diffusing at a higher rate originally were.

We did not take this circumstance into account, however, in deriving Eq. (3.19) for the diffusion coefficient, and this equation holds in essence only for the diffusion of gas molecules in a medium of the same gas. Such a process is called *self-diffusion*, and Eq. (3.19), consequently, expresses the *coefficient of self-diffusion*.

We have to do with such a phenomenon, for instance, when a gas mixture consists of two different isotopes of the same substance that only insignificantly differ from each other in their mass, but do not differ in any other

properties. If one of the isotopes is radioactive, it is easy to observe such self-diffusion because the penetration of the radioactive particles can be traced by their radiation.

### 3.9. COEFFICIENT OF INTERDIFFUSION

We can, however, correct Eq. (3.19) so that it will also hold for a mixture of two different gases. But to do this, we must take into account the existence of a compensating gas flow. We shall consider that Eq. (3.19) relates to one of the components of a mixture and characterizes the purely diffusion flux of this component:

$$M_1' = -\frac{1}{3}\bar{v}_1 l_1 \frac{d\rho_1}{dx} \tag{3.20}$$

The subscripts 1 indicate that the equation relates to the first component, and the prime used with the symbol for the mass indicates that $M_1'$ is the mass transported by diffusion. We must write an absolutely identical equation for the second component:

$$M_2' = -\frac{1}{3}\bar{v}_2 l_2 \frac{d\rho_2}{dx} \tag{3.21}$$

Here $d\rho_1/dx$ and $d\rho_2/dx$ are the gradients of the density of the first and second components along the $X$-axis. When the pressure throughout the entire volume is the same, the condition

$$\frac{d\rho_1}{dx} = -\frac{d\rho_2}{dx}$$

must be observed.

For the pressure of the gas to remain the same throughout the entire volume, the gas as a whole must start moving, and the velocity $u$ of this motion must be such that the gas flux $\rho u$ (where $\rho$ is the density of the mixture) will balance the surplus diffusion flux of the light-weight component, i.e. the equation

$$M_1' + M_2' + \rho u = 0 \tag{3.22}$$

should be obeyed.

Substituting for $M_1'$ and $M_2'$ in Eq. (3.22) their values from Eqs. (3.20) and (3.21), we get

$$-\rho u = -\frac{1}{3}\bar{v}_1 l_1 \frac{d\rho_1}{dx} - \frac{1}{3}\bar{v}_2 l_2 \frac{d\rho_2}{dx}$$

Or, since $d\rho_1/dx = -d\rho_2/dx$, then

$$-\rho u = \frac{1}{3}(\bar{v}_2 l_2 - \bar{v}_1 l_1)\frac{d\rho_1}{dx}$$

Hence,

$$u = -\frac{1}{3}\left(\frac{\bar{v}_2 l_2}{\rho} - \frac{\bar{v}_1 l_1}{\rho}\right)\frac{d\rho_1}{dx} \tag{3.23}$$

If the entire gas is moving, the masses of the first and second components actually intersecting a unit area do not equal $M_1'$ and $M_2'$ because both components are transported not only as a result of diffusion, but also as a result of the motion of the gas as a whole.

Hence, the mass of the first component intersecting a unit area equals $M_1' + \rho_1 u$ instead of $M_1'$, i.e.

$$M_1 = M_1' + \rho_1 u \tag{3.24}$$

Using instead of $M_1'$ and $u$ in Eq. (3.24) their values from Eqs. (3.20) and (3.23), we get

$$M_1 = \left(-\frac{1}{3} l_1 \bar{v}_1 - \frac{1}{3}\frac{\rho_1}{\rho} l_2 \bar{v}_2 + \frac{1}{3}\frac{\rho_1}{\rho} l_1 \bar{v}_1\right)\frac{d\rho_1}{dx}$$

or

$$M_1 = -\frac{1}{3}\left(\frac{\rho - \rho_1}{\rho} l_1 \bar{v}_1 + \frac{\rho_1}{\rho} l_2 \bar{v}_2\right)\frac{d\rho_1}{dx}$$

Since $\rho - \rho_1 = \rho_2$, then

$$M_1 = -\frac{1}{3}\left(\frac{\rho_2}{\rho} l_1 \bar{v}_1 + \frac{\rho_1}{\rho} l_2 \bar{v}_2\right)\frac{d\rho_1}{dx} \tag{3.25}$$

For the second component, similarly, we get

$$M_2 = -\frac{1}{3}\left(\frac{\rho_2}{\rho} l_1 \bar{v}_1 + \frac{\rho_1}{\rho} l_2 \bar{v}_2\right)\frac{d\rho_2}{dx} \tag{3.26}$$

Comparing these two equations with the diffusion equation (3.10), we see that the expressions before the density gradients [these expressions are identical in Eqs. (3.25) and (3.26)] are the diffusion coefficient. But now it is no longer the coefficient of self-diffusion, but the coefficient $D_{12}$ of diffusion of one gas into another *(interdiffusion)*:

$$D_{12} = \frac{1}{3}\left(\frac{\rho_2}{\rho} l_1 \bar{v}_1 + \frac{\rho_1}{\rho} l_2 \bar{v}_2\right) \tag{3.27}$$

The ratios $\rho_1/\rho$ and $\rho_2/\rho$ of the partial densities of the components to the density of the mixture are called the *relative concentrations* of the components.

It is easy to see that if the concentration of one of the components is low, Eq. (3.27) transforms into Eq. (3.19). If, for instance, the concen-

tration $\rho_1/\rho$ is low, then in Eq. (3.27) we may disregard the second term, while the concentration $\rho_2/\rho$ is close to unity. Consequently,

$$D_{12} = \frac{1}{3} l_1 \bar{v}_1 = D$$

Thus, Eq. (3.19) which we obtained in Sec. 3.8 holds not only for self-diffusion, but also for a mixture of various gases if one of the components is present in a small amount.

Using Eq. (3.19), we can assess the order of magnitude of the coefficient of diffusion (self-diffusion) for ideal gases.

For example for oxygen at atmospheric pressure, we have $l \approx 10^{-8}$ m and $\bar{v} \approx 5 \times 10^2$ m/s; hence, in these conditions, the diffusion coefficient will be

$$D = \frac{1}{3} l\bar{v} = \frac{1}{3} \times 10^{-8} \times 5 \times 10^2 \approx 1.67 \times 10^{-5} \text{ m}^2/\text{s}$$

The values of the interdiffusion coefficient for selected gases are given in Table 7.

*Table 7*

**Interdiffusion Coefficient for Selected Gases**

| Gases | $D_{12} \times 10^5$, m²/s | Gases | $D_{12} \times 10^6$, m²/s |
|---|---|---|---|
| $H_2$-$O_2$ | 6.79 | $CO_2$-$H_2$ | 5.38 |
| $O_2$-$N_2$ | 1.74 | $CO_2$-CO | 1.36 |
| CO-$H_2$ | 6.42 | $H_2O$-$CO_2$ | 0.98 |
| CO-$O_2$ | 1.83 | $H_2$-$D_2^*$ | 1.20 |

* $D_2$ stands for molecular deuterium (a hydrogen isotope whose molecular mass is double that of ordinary hydrogen).

**Measurement of the Diffusion Coefficient.** One of the simplest methods of measuring the diffusion coefficient was proposed by J. Loschmidt (1870). His apparatus consisted of two tubes placed one above the other and connected by a cock. The tubes were about 500 cm long and 2.6 cm in diameter.

An experiment is run in such an apparatus as follows. The tubes are filled with the gases to be studied with the cock closed. To prevent acceleration of the motion in diffusion by the action of the force of gravity, the heavier of the gases is introduced into the lower tube, and the lighter one into the upper tube.

Now we open the cock and one gas begins to penetrate into the other by diffusion. After a definite time, we again close the cock and analyse the

mixture obtained (it is naturally sufficient to analyse the contents of only one tube). The data of the analysis, the duration of the experiment, and the geometrical dimensions of the apparatus are all we need to calculate the coefficient of diffusion of one gas into the other.

An experiment run in such an apparatus with hydrogen and carbon dioxide showed, for instance, that in the thirty minutes during which the cock was open only 33% of the hydrogen penetrated into the lower tube. This is a striking illustration of the slow nature of a diffusion process at normal pressure!

Experiments conducted in apparatus similar to that described above also showed that the diffusion coefficient depends only slightly on the concentration of the components in the mixture. This indicates that Eq. (3.27) from which it follows that the diffusion coefficient must greatly depend on the concentration is not entirely accurate.

## 3.10. THERMAL DIFFUSION

The phenomenon of diffusion which we have just described appears when there is a difference (gradient) in the concentration of a component in a gas. Diffusion leads to vanishing of the gradient and transforms a heterogeneous gas mixture into a homogeneous one.

Another kind of diffusion called *thermal diffusion* (or *thermodiffusion*) exists in addition to such "concentration" diffusion. Thermal diffusion leads to the opposite result — to partial *separation* of a homogeneous gas mixture and its transformation into a heterogeneous one. This phenomenon was predicted theoretically in 1911 and discovered experimentally in 1917. The phenomenon of thermodiffusion consists in that a *difference in temperatures* in a homogeneous gas mixture causes the appearance of a *difference in concentrations* of the mixture components in the direction of lowering of the temperature.

Imagine a vessel with flat walls (Fig. 52*a*) filled with a homogeneous gas mixture. If its lower and upper walls are kept at the temperatures $T_1$

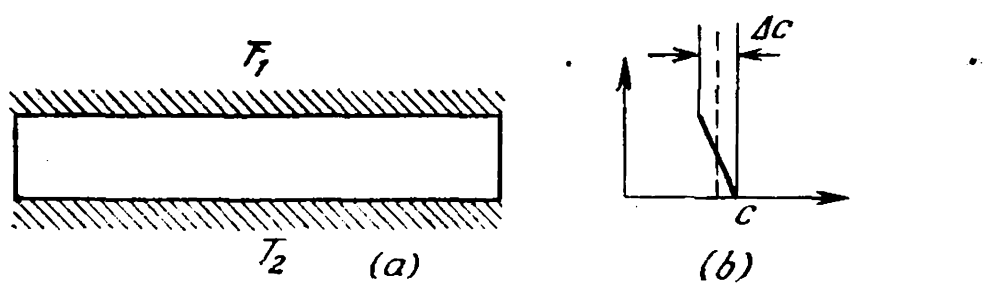



Fig. 52

and $T_2$, with $T_1 > T_2$, the phenomenon of thermodiffusion generally results in there being a surplus of *light* molecules at the *warmer* upper wall, and a surplus of *heavy* ones at the *colder* wall. The reverse direction of thermodiffusion is observed for some mixtures.

Figure 52*b* shows the distribution of the concentration $c$ of one of the components in height. The dash line shows the value of the concentration when there is no temperature difference. Thermodiffusion caused partial *separation* of the mixture into its components.

The difference in concentrations that appears tends to *level out* as a result of ordinary concentration *diffusion* whose flux is obviously directed opposite to the thermodiffusion flux. As a result of the joint action of these two processes, an *equilibrium gradient of concentrations* of the mixture components sets in.

The phenomenon of thermodiffusion cannot be explained by the simple molecular kinetic notions which we used with such success to explain ordinary diffusion (this is why thermodiffusion was not discovered for such a long time). It was found that an appreciable part in this phenomenon is played by forces of *repulsion* between molecules of the components upon their collision. It may be considered that these forces diminish with an increasing distance $r$ between the molecules according to the approximate law $F = f(1/r^n)$.

If the exponent $n$ exceeds five, thermodiffusion proceeds in the direction indicated above. If $n$ is less than five, the sign of the thermal diffusion difference in concentrations is reversed, and, finally, if $n$ equals five, thermodiffusion is in general impossible.

The change in the concentrations of the components of a mixture setting in as a result of thermodiffusion can be calculated with account taken of back diffusion.

Assume that the concentrations of the components of a mixture containing two gases equal $c$ and $1 - c$. By the concentration of a given component is meant the ratio of the number of molecules of this component to the total number of molecules in the mixture. Assume further that the temperature gradient $dT/dx$ is directed along the $X$-axis. Hence, as shown by theory, the gradient of concentration that sets in along the $X$-axis will be

$$\frac{dc}{dx} = \frac{D_T}{D_{12}} \frac{1}{T} \frac{dT}{dx} = \frac{D_T}{D_{12}} \frac{d}{dx} \ln T \qquad (3.28)$$

Here $D_{12}$ is the interdiffusion coefficient of the components, and $D_T$ is called the *thermal diffusion coefficient*; its dimension is obviously the same as that of $D_{12}$ (i.e. $m^2/s$). But unlike the interdiffusion coefficient $D_{12}$ which is virtually independent of the concentrations, the coefficient $D_T$ is proportional to the product of the concentrations of both components:

$$\frac{D_T}{D_{12}} = \alpha c(1 - c)$$

where $\alpha$ is the so-called *thermodiffusion constant*. It is exactly this constant $\alpha$ that depends on the properties of a mixture being separated, particularly on the exponent $n$ in the above-mentioned expression $F = f(1/r^n)$ — the

law of diminishing of the force of repulsion between molecules. The constant $\alpha$ also depends on the relative difference between the masses $m_1$ and $m_2$ of the molecules of a mixture. An approximate expression for $\alpha$ has the form

$$\alpha \approx \frac{m_2 - m_1}{m_2 + m_1} \frac{n-5}{n-1} \approx \frac{\Delta m}{2m} \frac{n-5}{n-1}$$

where $m$ is the mean value of the mass of a molecule. Hence, it is clear that the coefficient of thermodiffusion changes its sign when $n = 5$. For most gases $n > 5$. Equation (3.28) can now be rewritten in the form

$$\frac{dc}{dx} = \alpha c(1-c) \frac{d}{dx} \ln T \quad \text{or} \quad \frac{dc}{c(1-c)} = \alpha d \ln T$$

After integration, we get

$$\frac{c}{1-c} = AT^{\alpha}$$

The arbitrary constant $A$ can be eliminated if we take into account that $c = c_1$ when $T = T_1$, and $c = c_2$ when $T = T_2$. Hence,

$$\frac{c_1}{1-c_1} : \frac{c_2}{1-c_2} = \left(\frac{T_1}{T_2}\right)^{\alpha} \tag{3.29}$$

Equation (3.29) allows us to calculate the change in the relative concentrations of the components due to thermodiffusion, determine the constant $\alpha$, and thus establish the nature of the forces of interaction between molecules (see Chap. 5).

The phenomenon of thermal diffusion also has a great practical significance — it is used to separate isotopes.

The masses of isotopes generally differ from one another only slightly (exceptions are hydrogen and helium). This means that $\Delta m/2m \ll 1$ and, consequently, $\alpha \ll 1$. This permits us to simplify Eq. (3.29):

$$\frac{c_1}{1-c_1} : \frac{c_2}{1-c_2} = \exp\left\{\alpha \ln \frac{T_1}{T_2}\right\} \approx 1 + \alpha \ln \frac{T_1}{T_2} \tag{3.30}$$

The expression in the left-hand side of Eq. (3.30),

$$\frac{c_1}{1-c_1} : \frac{c_2}{1-c_2} = q$$

characterizes the degree of separation of the components and is called the *separation factor*. At low values of $\alpha$, i.e. for isotopes, the value of $q$ is close to unity (at $q = 1$ there is no separation at all). Therefore, the degree of separation is often characterized by the quantity $q - 1 = \varepsilon$ called the *enrichment factor*. It is quite obvious that

$$\varepsilon = \alpha \ln \frac{T_1}{T_2} \approx \frac{\Delta m}{2m} \ln \frac{T_1}{T_2}$$

For example for neon isotopes with atomic weights of $\mu_1 = 20$ and $\mu_2 = 22$, and for temperatures of $T_1 = 900\,°C$ and $T_2 = 300\,°C$, the enrichment factor is $\varepsilon \approx 0.03$. This means that the initial concentration changes by only 3% as a result of thermodiffusion.

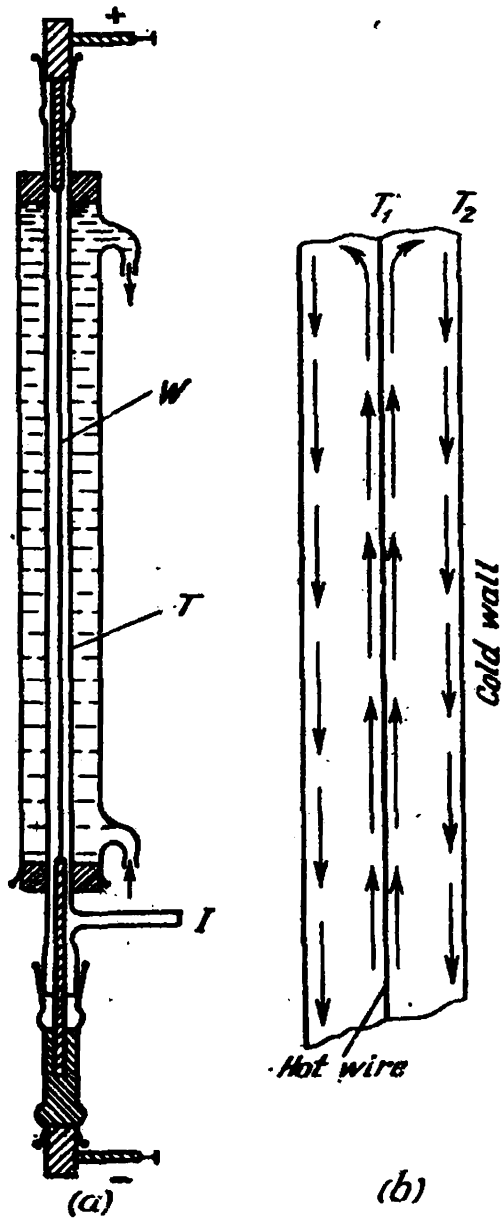



Fig. 53

This circumstance prompted scientists to find ways of increasing the degree of enrichment caused by thermodiffusion. Such a way was found. It consists in that the difference in temperatures ensuring thermal diffusion was used for creating a *convection* flow of a gas mixture. As a result of such convection, the heated portion of a gas moves relative to the cold portion and forms a "counterflow". For this purpose, the temperature gradient must be directed horizontally so that the force of gravity can be used to create vertical convection. This principle was embodied in the "separating column" shown schematically in Fig. 53*a*. Metal wire *W* heated by an electric current is stretched along the axis of vertically installed tube *T* cooled by running water. The gas mixture to be enriched is introduced via inlet tube *I*. The temperature of the gas near the wire is higher than at the walls of the tube, and this induces thermodiffusion.

Let us see how the degree of separation increases in this apparatus. Thermal diffusion results in the gas near the hot wire becoming richer in the light component, and near the cold wall in the heavy one. Further, the gas near the hot wire expands, its density therefore diminishes and it rises, while the cold gas near the tube walls lowers. A circulation flow of the gas appears which is directed as shown by the arrows in Fig. 53*b*. It is obvious that such circulation *lifts* a greater number of the light molecules than it *lowers* at the cold wall, although the summary flows of the gas upward and downward are absolutely the same. As a result, a surplus of the light component accumulates in the upper part of the apparatus, and a surplus of the heavy component in its lower part.

Thermodiffusion "feeds" the light molecules toward the hot wire, and convection "carries them away" upward. A *vertical* concentration gradient

is formed as a result. Separation is many times greater than in pure thermal diffusion separation.

A considerable number of isotopes were separated in this way. The thermal diffusion method of separation has not found broad industrial application, notwithstanding its simplicity. This is explained by the too great consumption of heat energy that attends the process of thermodiffusion.

There is still another kind of diffusion called *forced diffusion*. It appears in a gas mixture under the action of a pressure difference. Forced diffusion also results in the separation of gas mixtures. This method by itself, however, has found no practical application.

## 3.11. THERMAL CONDUCTIVITY OF GASES

If a gas is heated unevenly, i.e. the temperature in one portion of it is higher or lower than in another portion, levelling out of the temperature is observed: the hotter portion cools and the colder part becomes heated.

This is evidently connected with the flow of heat from the warmer portion of the gas to the colder one. This phenomenon of the appearance of a heat flux in a gas (or in any other substance) is called *thermal conductivity*. When any body, particularly a gas, is left to itself, thermal conductivity leads to levelling out of the temperatures, and this process is naturally not stationary. Cases are often encountered, however, when a temperature difference is kept constant artificially.

For instance in an incandescent lamp, the gas directly near the glowing filament has a high temperature (equal to that of the filament itself) whereas the gas adjoining the walls of the glass bulb of the lamp has a considerably lower temperature. In a certain time after the lamp has been switched on, a constant temperature difference sets in between the filament and the walls. This is ensured on the one hand by the electric energy supplied to the filament from the mains and on the other by the removal of heat from the walls of the lamp to the air surrounding it. In these conditions, a stationary (steady-state), i.e. unchanging with time, flow of heat sets in in the gas contained in the lamp. The stationary temperature difference that sets in depends on the thermal conductivity of the gas (it must be borne in mind that in incandescent lamps, apart from the removal of heat through the gas, heat is mainly removed by radiation).

In the above example of a lamp, calculations of the heat flux involve great difficulties connected with the intricate shape of the filament and the bulb. As a result, the distribution of the temperature in the gas is also very complicated.

To find the quantitative laws characterizing the process of thermal conductivity, we shall consider a simpler problem similar in nature to the one we dealt with when studying diffusion.

Assume that along any direction in a gas, for example along the $X$-axis, the temperature changes from point to point, i.e. is a function of $x$ whereas

the temperature is identical at any point in a plane at right angles to this axis (Fig. 54).

The change in temperature along the $X$-axis is characterized by the temperature gradient $\partial T/\partial x$ (if the temperature, as we assumed, changes only along the $X$-axis, then we can write $dT/dx$ instead of $\partial T/\partial x$). As in all cases, the meaning of the temperature gradient consists in that it equals the change in the temperature from one point to another related to a unit distance between them. The existence of a temperature gradient is an essential condition for the appearance of thermal conductivity, just like the existence of a concentration gradient is needed for diffusion to occur.

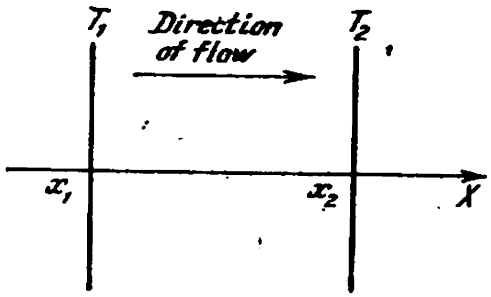


Fig. 54

The direction of the heat flux coincides with that of the drop in temperature. If a drop in temperature ($dT < 0$) corresponds to a growth in $x$ (i.e. $dx > 0$), the heat flows in the direction of growing $x$: the heat flux is directed so as to diminish the existing temperature gradient that caused it to appear. Experiments show that the heat flux $Q$ is proportional to the temperature gradient (the Fourier law):

$$Q = -\lambda \frac{dT}{dx} \tag{3.31}$$

By the heat flux, we shall again understand the quantity of heat flowing through a unit area in a unit time.

The coefficient $\lambda$ in Eq. (3.31) is called the *coefficient of thermal conductivity*. Inspection of Eq. (3.31) shows that it numerically equals the heat flux at a temperature gradient equal to unity (1 K/cm). The thermal conductivity coefficient in the SI system is expressed in J/m·s·K or in W/m·K, and in the cgs system in erg/cm·s·K. In engineering, it is often expressed in kJ/m·h·K.

In steady-state conditions, the quantity of heat $Q$ flowing in a unit time through a gas equals the power of the source of energy at whose expense the given temperature gradient is maintained. It is exactly this power (usually electrical) that is to be measured in the experimental determination of the coefficient of thermal conductivity (see below).

When a gas in which there is a temperature gradient is left alone, i.e. no energy is supplied to it from outside, thermal conductivity results in levelling out of the temperature. We shall first consider such *non-stationary* thermal conductivity. We shall see that the law of levelling out of the temperature reminds us quite closely of the process of levelling out of the concentration by diffusion.

## 3.12. NON-STATIONARY THERMAL CONDUCTIVITY

Let us again consider two vessels *I* and *II* (see Fig. 50) whose volumes are $V_1$ and $V_2$, respectively. They are now filled with a gas homogeneous in composition, and the pressure in both vessels is the same. The two vessels are connected by a tube with a length of $l$ and a cross-sectional area of $A$. Let the temperatures of the gas in our vessels at a certain moment be $T_1$ and $T_2$, and to avoid ambiguity assume that $T_1 > T_2$.

If we now leave the gas alone, owing to thermal conductivity the temperature of the gas in the two vessels will level out, i.e. the temperature difference $\Delta T = T_1 - T_2$ will diminish with time. This process could be called "temperature diffusion". Here, however, diffusion in the conventional meaning of the word also occurs. If the temperature of the gas in one of the vessels is higher than in the other, this means that there are more molecules with a high velocity in the vessel with the higher temperature than in the other one because temperature is determined by the mean kinetic energy of the molecules, and this energy is the greater, the more there are molecules with high velocities. The process of thermal conductivity is naturally attended by diffusion of these more rapid particles, and it plays an important part in the mechanism of thermal conductivity.

Let us now find the law of diminishing of the temperature difference with time. By Eq. (3.31), the flow of heat through the tube is

$$Q = -\lambda \frac{dT}{dx}$$

To simplify our reasoning, we shall assume that the temperature along the connecting tube changes uniformly so that the same temperature difference falls to any unit length. Consequently, there is no need to use infinitesimals, and we can write

$$\frac{dT}{dx} = \frac{\Delta T}{l} \quad \text{and} \quad Q = -\lambda \frac{\Delta T}{l}$$

During the infinitely small time $dt$, a quantity of heat equal to

$$dQ = -\lambda \frac{\Delta T}{l} A\, dt \tag{3.32}$$

will pass from vessel *I* to vessel *II* through the tube. As a result, the temperature of the gas in vessel *I* will lower by a certain amount $dT_1$, and in vessel *II* it will rise by the amount $dT_2$. By exactly how much the temperature will rise in vessel *II* and lower in vessel *I* depends on the heat capacity of the gas $C$ equal to the product of the specific heat capacity of the gas $c_V$ and its mass $m$. From previously discussed relationships between the quantity of heat and the change in the temperature, it is clear that

$$dT_1 = \frac{dQ}{m_1 c_V}, \quad dT_2 = \frac{dQ}{m_2 c_V}$$

where $m_1$ and $m_2$ = masses of the gas in vessels $I$ and $II$, respectively
$dT_1$ and $dT_2$ = absolute values of the changes in the temperature.
If the density of the gas in the vessels is $\rho$, then

$$m_1 = \rho V_1, \qquad m_2 = \rho V_2$$

and, therefore,

$$dT_1 = \frac{dQ}{\rho V_1 c_V}, \quad dT_2 = \frac{dQ}{\rho V_2 c_V}$$

The drop in the temperature in vessel $I$ by $dT_1$ and its increase in vesse $II$ by $dT_2$ result in diminishing of the temperature difference between them by the amount

$$d(\Delta T) = dT_1 + dT_2 = \frac{dQ}{\rho c_V}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) = \frac{dQ}{\rho c_V}\frac{V_1 + V_2}{V_1 V_2}$$

Substitution for $dQ$ of its value from Eq. (3.32) yields

$$d(\Delta T) = -\frac{\lambda A \Delta T}{l \rho c_V}\frac{V_1 + V_2}{V_1 V_2}\, dt$$

We denote as previously the reduced volume $V_1 V_2/(V_1 + V_2)$ by $V_0$. Hence,

$$d(\Delta T) = -\frac{\lambda A \Delta T}{l \rho c_V V_0}\, dt \quad \text{or} \quad \frac{d(\Delta T)}{\Delta T} = -\frac{\lambda A}{l \rho c_V V_0}\, dt$$

Integration of this equation gives

$$\ln \Delta T = -\frac{\lambda A}{l \rho c_V V_0} t + \ln I \tag{3.33}$$

where $I$ is an integration constant. It can easily be determined by making use of the circumstance that the temperature difference at the initial moment, i.e. at $t = 0$, equals $(\Delta T)_0$. Using $t = 0$ and $\Delta T = (\Delta T)_0$ in Eq. (3.33), we get $I = (\Delta T)_0$. Consequently,

$$\Delta T = (\Delta T)_0 \exp\left(-\frac{\lambda A}{l \rho c_V V_0} t\right) \tag{3.34}$$

Equation (3.34) expresses the law of levelling out of the temperature with time as a result of thermal conductivity which we are interested in. This law is similar to that of levelling out of the concentration by diffusion [Eq. (3.16)]. In both cases, levelling out occurs according to an exponential law.

If we compare Eq. (3.34) with Eq. (3.16), i.e.

$$\Delta n = (\Delta n)_0 \exp\left(-D \frac{A}{V_0 l} t\right)$$

we see that the exponential factors in the right-hand side of both equations coincide if we assume that

$$\frac{\lambda}{\rho c_V} = D$$

This means that the expression $\lambda/\rho c_V$ is the coefficient of "temperature diffusion". The quantity $\lambda/\rho c_V$, which depends on the properties of a gas, characterizes the rate of levelling out of the temperature. This quantity was therefore called the *coefficient of temperature conductivity of a gas* (or of any other body).

The factor $A/V_0 l$ is purely geometric and characterizes only the apparatus.

It is not difficult to see that the coefficient of temperature conductivity, like the diffusion coefficient, is expressed in $m^2/s$.

As when considering diffusion, we shall introduce the *time constant* of thermal conductivity

$$\tau = \frac{\rho c_V}{\lambda} \frac{l V_0}{A} \tag{3.35}$$

This is the interval of time during which the difference in temperatures between two volumes decreases $e$ times as a result of thermal conductivity.

## 3.13. STATIONARY THERMAL CONDUCTIVITY. CALCULATION OF THE THERMAL CONDUCTIVITY COEFFICIENT

As a result of the thermal motion of gas molecules, any cross section in a volume occupied by a gas is intersected by molecules. Let us consider, as we have previously done, a certain area $A$ (Fig. 55) at right angles to the $X$-axis along which a constant temperature difference is maintained (the process is stationary). Assume that $T_1$ is greater than $T_2$.

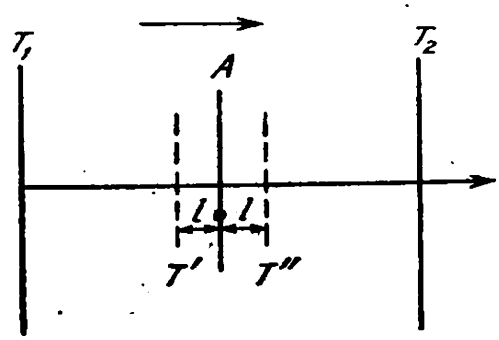


Fig. 55

Molecules pass through area $A$ both from left to right and from right to left. If the pressure of the gas at all points is the same, the number of molecules intersecting a unit of area $A$ in one second from the left and the right is obviously identical. But the molecules arriving from the left carry along more energy than those arriving at the area from the right because they have come from a region having a higher temperature. Consequently, a heat flux appears (from left to right) equal to the difference between the energies transported by the molecules from the left and from the right.

We can assume as previously that the number of molecules $N_1$ intersecting 1 cm² of the area in one second from left to right equals $\frac{1}{6} n\bar{v}$. In exactly the same way, $N_2$ molecules cross the area from right to left; here $N_2 = \frac{1}{6} n\bar{v}$. In these expressions, $\bar{v}$ is the mean velocity of the thermal motion of molecules, and $n$ is the number of molecules in a unit volume. As we have just noted, the numbers of molecules $N_1$ and $N_2$ are the same, but they carry different amounts of energy. Let us now find these amounts.

The molecules arriving at area $A$ from the left reach it with the energy they had after the last collision before it. The free path is different for different molecules, but for a comparatively rough assessment we may assume that all the molecules reaching area $A$ had their last collision at a distance from it equal to the mean free path $l$. We can also consider, accordingly, that the molecules arriving at the area from the left have the mean energy $U_1$ corresponding to the temperature $T'$ at a point that is to the left of area $A$ by the distance $l$. The quantity of energy brought to 1 cm² of the area by these molecules in one second is

$$Q_1 = \frac{1}{6} n\bar{v} U_1$$

Similarly, the quantity of energy brought by the molecules arriving from the right is

$$Q_2 = \frac{1}{6} n\bar{v} U_2$$

where $U_2$ is the energy of the molecules corresponding to the temperature $T''$ at a point that is to the right of area $A$ by the distance $l$. Consequently, the resulting quantity of energy flowing through 1 cm² of the area in one second is

$$Q = Q_1 - Q_2 = \frac{1}{6} n\bar{v}(U_1 - U_2) \tag{3.36}$$

where $U_1$ and $U_2$ are the mean values of the energy of a molecule corresponding to the temperatures $T'$ and $T''$ at points at a distance of $2l$ from each other.

The mean energy of a molecule $U$ is proportional to the temperature, and can be expressed through the heat capacity of a gas $C_V$.

Indeed, the mean energy of a molecule is $(i/2)kT$, where $i$ is the number of degrees of freedom, and $k$ is the Boltzmann constant. On the other hand, the molar heat capacity of a gas $C_V = (i/2)R = (i/2)kN_A$, where $N_A$ is the Avogadro constant. Hence,

$$U = \frac{i}{2} kT = \frac{C_V}{N_A} T$$

Equation (3.36) can therefore be rewritten in the form

$$Q = \frac{1}{6} n\bar{v} \frac{C_V}{N_A} (T' - T'')$$

It is not difficult to determine the temperature difference $T' - T''$ between points at both sides of area $A$ at a distance of $l$ from it from the value of the temperature gradient

$$T' - T'' = -2l \frac{dT}{dx}$$

because the temperature gradient $dT/dx$ is the change in temperature per unit length. The minus sign shows that an increase in $x$ is attended by diminishing of $T$. Hence,

$$Q = -\frac{1}{3} n\bar{v}l \frac{C_V}{N_A} \frac{dT}{dx} \tag{3.37}$$

Comparing Eqs. (3.37) and (3.31), we get an expression for the coefficient of thermal conductivity:

$$\lambda = \frac{1}{3} n\bar{v}l \frac{C_V}{N_A} \tag{3.38}$$

If we take into account that $C_V = \mu c_V$, where $c_V$ is the specific heat capacity, $\mu$ is the molecular mass, and $\mu/N_A = m$ is the mass of one molecule, then Eq. (3.38) can be rewritten in the form

$$\lambda = \frac{1}{3} mn\bar{v}lc_V = \frac{1}{3} \rho\bar{v}lc_V \tag{3.39}$$

where $\rho$ is the density of a gas equal to $mn$ (the product of the mass of a molecule and the number of molecules in a unit volume).

Equations (3.38) and (3.39) give only an approximate value of the coefficient of thermal conductivity of a gas because the numerical factor in them depends on the assumptions made in our calculations and only approximately equals one-third. The accurate calculation of this factor involves great difficulties.

**Pressure and Temperature Dependence of Coefficient of Thermal Conductivity.** The above equations (3.38) and (3.39) allow us to see how the coefficient of thermal conductivity should depend on the pressure and the temperature of a gas.

Among the quantities in Eqs. (3.38) and (3.39), only the number of molecules in a unit volume $n$ and the free path $l$ depend on the pressure. But the first of these two quantities is proportional, and the second inversely proportional to the pressure of a gas. This leads to the important conclusion that the coefficient of thermal conductivity of gases does not depend on the pressure.

This conclusion, which seems paradoxical at first sight, agrees excellently with experimental data, however. The latter show that the coefficient of thermal conductivity remains unchanged when the pressure of a gas is changed within broad limits. And only at very low pressures does the coefficient of thermal conductivity begin to diminish with lowering of the pressure. We shall see below that this circumstance does not at all contradict the above notions on the mechanism of thermal conductivity.

*As regards the temperature dependence, it follows from* Eq. (3.39) that the coefficient of thermal conductivity, which is proportional to the mean velocity of thermal motion of molecules, should vary with the temperature in the same way as $\bar{v}$, i.e. in proportion to $\sqrt{T}$.

*Actually, the coefficient of thermal* conductivity, as shown by experiments, grows with the temperature at a somewhat higher rate than in proportion to $\sqrt{T}$. This should be expected because the coefficient of thermal conductivity is also proportional to the mean free path, and this quantity also grows with increasing temperature. For polyatomic gases, account must also be taken of the growth in heat capacity with temperature.

The growth of the free path with increasing temperature is connected with the fact that molecules cannot be treated as rigid spheres. This is confirmed by the experimentally established quicker growth of the coefficient of thermal conductivity with temperature than in proportion to $\sqrt{T}$.

**Coefficient of Thermal Conductivity and Size of Molecules.** Equation (3.38) can be transformed by substituting for $l$ its value from Eq. (3.4). Hence, the expression for the coefficient of thermal conductivity becomes

$$\lambda = \frac{\bar{v} C_V}{3\sqrt{2}\sigma N_A} \qquad (3.40)$$

where $\sigma = 4\pi r^2$.

The quantities $\bar{v}$ and $C_V$ are generally known from other sources. Therefore, Eq. (3.40) can be used to assess the cross-sectional area $\sigma$ or the radius of a molecule $r$ if the value of the coefficient of thermal conductivity has been measured.

For example, according to the results of measurements, the coefficient of thermal conductivity for oxygen at 0 °C equals 0.024 W/m·K. Using the known values of $\bar{v}$ and $C_V$, we get

$$\sigma = \frac{\bar{v} C_V}{3\sqrt{2}\lambda N_A} \approx \frac{5 \times 10^2 \times 20.9}{3 \times 1.4 \times 0.024 \times 6.02 \times 10^{23}} = 1.7 \times 10^{-19}\ \text{m}^2$$

Hence, the radius of a molecule is

$$r = \sqrt{\frac{\sigma}{4\pi}} \approx 1.4 \times 10^{-10}\ \text{m}$$

The size of the molecules of most gases is of the same order of magnitude, as can be seen from Table 8.

*Table 8*

| Gas | Diameter of molecules, m | Gas | Diameter of molecules, m |
|---|---|---|---|
| Hydrogen | $2.74\times10^{-10}$ | Oxygen | $3.61\times10^{-10}$ |
| Helium | $2.18\times10^{-10}$ | Argon | $3.64\times10^{-10}$ |
| Nitrogen | $3.75\times10^{-10}$ | | |

Thus, among the quantities in Eq. (3.40) for the coefficient of thermal conductivity, $C_V$ and $\sigma$ are approximately the same for all ideal gases. Therefore, the difference in the values of the coefficient of thermal conductivity can be explained only by the difference in the values of the mean velocity of the molecules $\overline{v}$. Since the velocity $\overline{v}$ of molecules at a given temperature depends on their mass, we should expect light gases whose molecules have a higher velocity of thermal motion to have a greater coefficient of thermal conductivity than heavy gases. This is well confirmed experimentally, as can be seen from Table 9 which gives experimental data on the coefficients of thermal conductivity of selected gases.

*Table 9*

| Gas | $\lambda$, W/m·K | Gas | $\lambda$, W/m·K |
|---|---|---|---|
| Hydrogen | 0.176 | Oxygen | 0.024 |
| Helium | 0.142 | Carbon dioxide | 0.014 |

Hydrogen, owing to its good thermal conductivity, is used for cooling various industrial units when water cooling is out of the question for some reason or other, for example in large turbogenerators.

If the size of the molecules of a gas is known from other measurements, then measurement of the thermal conductivity permits us to find the value of $\sigma$. The size of molecules can naturally also be calculated from other transport coefficients.

**Measurement of the Coefficient of Thermal Conductivity.** Difficulties are generally introduced into the experimental studying of the thermal conductivity of gases by the fact that the transfer of heat in a gas may occur not only by the mechanism of thermal conductivity described above, but also by the so-called free convection which easily originates in a gas. *Convection* is the transfer of heat together with the transport of the mass of a gas under the action of gravitational forces in the presence of a temperature difference. Convection, like thermal conductivity, tends to level out

the temperature in a gas. This is why it is difficult to distinguish between these two mechanisms of heat transfer in experiments, and when measuring the thermal conductivity, such conditions must be ensured in which no convection is possible. One of the most widespread ways of measuring the coefficient of thermal conductivity of gases consists in the following (Schleiermacher, 1888).

The space between two coaxial cylinders having radii of $r_1$ and $r_2$ (Fig. 56) is filled with the gas to be studied. One of the cylinders (almost always the inner one) is heated by an electric heater consuming the power $P$ while the other cylinder is cooled so that its temperature $T_2$ remains constant all the time. The inner cylinder, particularly, may be simply a thin wire or filament along which an electric current is passed so that it also is a heater (Fig. 57).

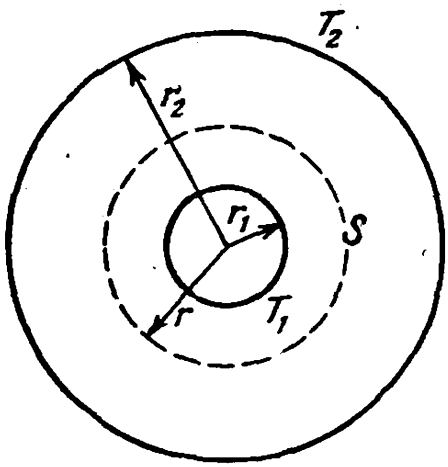



Fig. 56

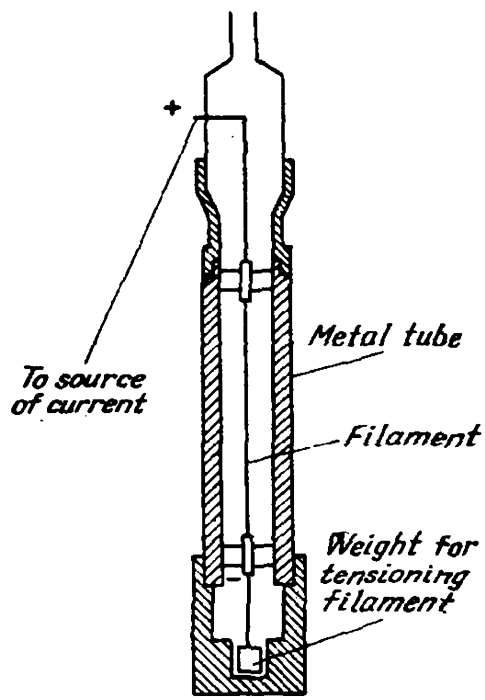



Fig. 57

In a certain time after the heater has been switched on, a stationary state sets in at which the temperature $T_1$ of the inner heated cylinder also becomes constant. Thus a constant temperature difference $T_1 - T_2$ sets in between the inner and outer cylinders. The magnitude of this temperature-difference depends on the thermal conductivity of the gas. It is not difficult to find this relationship.

If the altitude of a cylinder is $h$ (to avoid an error connected with convection, the apparatus should be set up vertically), the quantity of heat flowing in one second through any cylindrical cross section $A$ having the radius $r$ (i.e. $A = 2\pi rh$) is determined by the equation

$$Q = -\lambda \frac{dT}{dr} A$$

where $dT/dr$ is the temperature gradient along the radius of the cylinder. If the altitude of the cylinder is sufficiently great in comparison with its radius, the temperature along the axis of the cylinder may be considered to be the same everywhere.

In a stationary state, $Q$ equals the power of the heater $P$. Consequently,

$$P = -2\pi r h \lambda \frac{dT}{dr}$$

whence

$$\frac{dT}{dr} = -\frac{P}{2\pi\lambda h}\frac{1}{r} \quad \text{or} \quad dT = -\frac{P}{2\pi\lambda h}\frac{dr}{r}$$

Integration yields

$$T = -\frac{P}{2\pi\lambda h}\ln r + C$$

where $C$ is an integration constant. It can be found from the condition that the temperature $T = T_1$ when $r = r_1$ and $T = T_2$ when $r = r_2$, i.e.

$$T_1 = -\frac{P}{2\pi\lambda h}\ln r_1 + C, \quad T_2 = -\frac{P}{2\pi\lambda h}\ln r_2 + C$$

and

$$T_1 - T_2 = \frac{P}{2\pi\lambda h}\ln\frac{r_2}{r_1} \tag{3.41}$$

Thus, the steady-state temperature of the cylinder being heated is

$$T_1 = T_2 + \frac{P}{2\pi\lambda h}\ln\frac{r_2}{r_1}$$

Having measured the temperatures $T_1$ and $T_2$ and knowing the geometrical dimensions of the apparatus and the power of the heater, we can calculate the coefficient of thermal conductivity:

$$\lambda = \frac{P}{2\pi h(T_1 - T_2)}\ln\frac{r_2}{r_1} \tag{3.42}$$

## 3.14. VISCOSITY OF GASES (INTERNAL FRICTION)

The viscosity of gases (this also relates to liquids) is a property owing to which the velocities of different layers of a gas level out. We owe the fact that a wind or a storm abates with time, for example, to this property. The velocities of adjacent layers of a gas level out, if these velocities are different, because the impulse (momentum) is transferred from the layer of the gas having a higher velocity to the layer with the lower velocity.

If a constant difference between the velocities of different layers of a gas is maintained by external forces, then the flux of the impulse from layer

to layer will also be constant (stationary) and this flux will be directed along the drop in velocity. We encounter such a case, for example, in the slow flow of a gas (or liquid) between two plates or in a tube or pipe under the action of a constant external difference of pressures directed along the motion.

When a gas flows along a tube, the velocities of the different layers are distributed as shown in Fig. 58 where the arrows are gas velocity vectors. The highest velocity is observed in the middle of the tube along its axis. The velocity diminishes as we approach the walls, and the layer directly adjoining the walls of the tube is at rest.

With such flow, the pulse is transferred from the central layer of the gas where the velocity is the highest to the layers moving with a lower velocity. Since this process is connected with a change in the momentum, the gas behaves as if a certain force (the force of internal friction) acted on it.

The transfer of the impulse can be described quantitatively in the same way as we described the transfer of energy in the process of thermal conductivity.

Assume that the change in the velocity of a gas occurs in the direction of the $X$-axis, which in the given case is perpendicular to the direction of the velocity of the gas itself (Fig. 59).

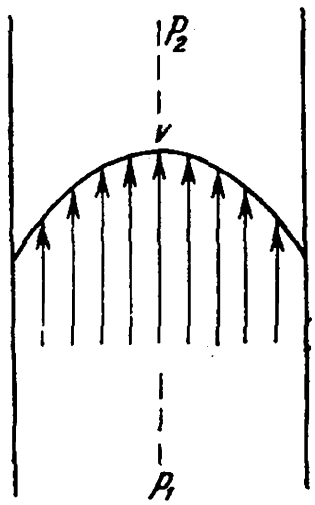



Fig. 58

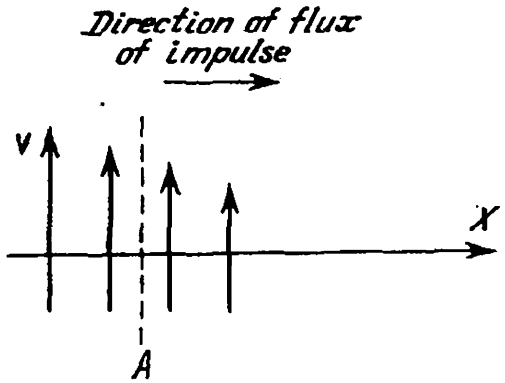



Fig. 59

In the direction perpendicular to the $X$-axis, the velocity at all points is the same. This means that the velocity $v$ is a function only of $x$. Hence, as shown by experiments, the momentum $\bar{p}$ transported during one second through 1 cm$^2$ of a cross section perpendicular to the $X$-axis will be determined by the equation

$$\bar{p} = -\eta \frac{dv}{dx} \qquad (3.43)$$

where $dv/dx$ is the gradient of the velocity along the $X$-axis, which characterizes the rate of change in the velocity along this axis (the change in

velocity per unit length). The minus sign signifies that the impulse is transported in the direction of a reduction in velocity.

The factor $\eta$ is called the *viscosity* or the *coefficient of internal friction* of a gas, and, like the coefficients of diffusion and thermal conductivity, depends on the properties of the gas. Sometimes the quantity $\eta$ determined with the aid of Eq. (3.43) is called the dynamic viscosity as distinct from the kinematic viscosity equal to the ratio $\eta/\rho$, where $\rho$ is the density of the gas (this quantity will be discussed on a later page).

The physical meaning of the viscosity consists in that it is numerically equal to the momentum transported in a unit time (1 s) through an area of 1 $cm^2$ at a velocity gradient (in a direction perpendicular to the area) equal to unity (1 cm/s per cm of length).

The unit of viscosity in the SI system of units is the viscosity of a substance (gas) in which a momentum of 1 kg·m/s is transported through an area of 1 $m^2$ in one second with the velocity gradient equal to unity (1 $s^{-1}$). Consequently, the viscosity is measured in the units kg/m·s. In the cgs system, the viscosity is measured in g/cm·s. This unit is called the *poise* (P). The kinematic viscosity is correspondingly measured in $m^2/s$ and $cm^2/s$. The latter unit is called the *stokes* (St).

When an impulse is transported from layer to layer, the impulse of these layers changes (grows or diminishes). This means that a force equal to the change in the impulse in a unit time acts on each of the layers (Newton's second law). We know that $\bar{p}$ in Eq. (3.43) is the transport of the impulse in a unit time! Therefore, viscosity results in the fact that any layer of a gas moving relative to the adjacent one is subjected to the action of a force.

This force is the force of friction between the layers of a gas moving with different velocities. Hence the name *internal friction*. Equation (3.43) can therefore also be written in the form

$$F = -\eta \frac{dv}{dx} \tag{3.44}$$

where $F$ is the force acting on a unit area of the surface separating two adjacent layers of a gas. The viscosity is numerically equal to the force acting on a unit area at a velocity gradient equal to unity.

Internal friction is the reason why a certain pressure difference is needed for a gas (or liquid) to flow through a tube or pipe. For the velocity of the stream to have a certain given value, this pressure difference must be the greater, the greater is the coefficient of internal friction $\eta$.

The relationship between the volume $V$ of a gas flowing in a unit time through a cross section of a tube and the pressure difference $\Delta p$ needed for this is established by the well-known Poiseuille formula

$$V = \frac{\pi R^4}{8\eta} \frac{\Delta p}{L} \tag{3.45}$$

where $L$ = length of the tube
$R$ = its radius.

We can use this formula to determine the viscosity of a gas if we measure the volume of the gas flowing through a tube in a certain time, the difference between the pressures at its ends, and know the geometrical dimensions of the tube.

**Calculating the Viscosity of Gases.** The viscosity of a gas can be assessed in the same way as we used in calculating the coefficients of thermal conductivity and diffusion.

If a gas flows with a certain velocity $v$, this means that all its molecules have this velocity superposed on the velocity of thermal motion, which proceeds in a flowing gas in absolutely the same way as in one at rest. Each molecule therefore has the impulse or momentum $mv$ ($m$ is the mass of a molecule) in the same direction for all the molecules. Usually the flow velocity of a gas is considerably lower than the mean velocity of thermal motion of its molecules. *

Let us consider area $A$ parallel to the flow velocity of a gas and, therefore, perpendicular to the direction of transport of the impulse (Fig. 60). Assume that the flow velocity of the gas diminishes in the direction of the $X$-axis, i.e. the flow velocity to the right of the area is lower than to the left of it. Owing to the exchange of molecules between the two layers of the gas (the exchange occurs because of thermal motion), this difference decreases. The molecules to the right of $A$ are replaced by other molecules arriving from the left which have a higher velocity and, therefore, a greater impulse. When these molecules collide with the ones that had been to the right of $A$ before this happened, the higher flow velocity will be distributed among all the molecules to the right, after which the flow velocity of this layer and, consequently, the impulse, will become greater whereas the velocity and impulse of the layer of the gas to the left of $A$ decrease.

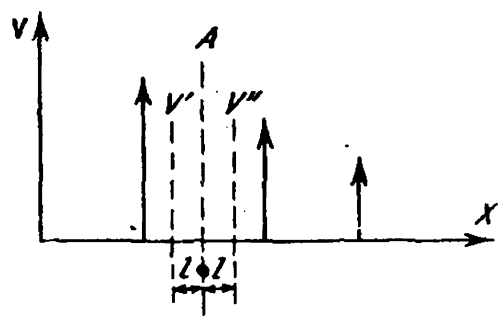


Fig. 60

In other words, the exchange of molecules due to thermal motion results in levelling out of the flow velocities of different layers of the gas. This is the mechanism of transport of the impulse in the direction of the $X$-axis from one layer of a flowing gas to another.

The impulse flux $\bar{p}$ transferred in a unit time (1 s) through a unit area of section $A$ is determined by the difference between the impulses $\bar{p}_1$ and $\bar{p}_2$ transported by the molecules crossing area $A$ from the left and from the

*When the velocity of a gas flow is greater than that of the thermal motion of molecules (more exactly, greater than the velocity of sound in a given gas), a number of new phenomena appear forming the subject studied by *gas dynamics*.

right. The impulse $\bar{p}_1$ transported by the molecules from left to right equals the product of the impulse of a separate molecule and the number of molecules intersecting a unit area in a unit time. The latter, as shown above, equals $\frac{1}{6} n\bar{v}$ (here $n$ is the number of molecules in a unit volume, and $\bar{v}$ is the mean velocity of thermal motion of a molecule). The impulse of a separate molecule which it brings along when crossing area $A$ is the impulse which the molecule had in the last collision before the area, i.e. at a distance of the order of magnitude of the mean free path $l$ from area $A$.

If the flow velocity of a gas at the distance $l$ to the left of $A$ equals $v'$, then the impulse of a molecule connected with the flow of the gas equals $mv'$ ($m$ is the mass of a molecule). Thus

$$\bar{p}_1 = \frac{1}{6} n\bar{v}mv'$$

For the molecules crossing area $A$ from the right, correspondingly,

$$\bar{p}_2 = \frac{1}{6} n\bar{v}mv''$$

where $v''$ is the flow velocity of the gas at a distance $l$ to the right of $A$. The resultant impulse flux $\bar{p}$ through a unit area in one second is

$$\bar{p} = \bar{p}_1 - \bar{p}_2 = \frac{1}{6} mn\bar{v}(v' - v'')$$

where $v' - v''$ is the difference between the flow velocities of the gas at points that are at a distance of $2l$ from each other, i.e.

$$v' - v'' = -2l \frac{dv}{dx}$$

whence

$$\bar{p} = -\frac{1}{3} mn\bar{v}l \frac{dv}{dx} \tag{3.46}$$

Comparing this expression with Eq. (3.43), we get an expression for the viscosity:

$$\eta = \frac{1}{3} mn\bar{v}l = \frac{1}{3} \rho\bar{v}l \tag{3.47}$$

where $\rho$ is the density of the gas.

Equation (3.47), like the value of the coefficient of thermal conductivity obtained on an earlier page, assesses the viscosity with an accuracy to the numerical factor, which only approximately equals 1/3.

Inspection of Eq. (3.47) shows that the viscosity should also remain independent of the pressure because the product $\rho l$ does not depend on the pressure. Experiments involving measurement of the viscosity within a broad range of pressures have confirmed this conclusion.

A comparison of the expressions for the coefficient of thermal conductivity (3.39) and the viscosity (3.47) shows that there is a simple relationship between them:

$$\lambda = \eta c_V \tag{3.48}$$

where $c_V$ is the specific heat capacity at constant volume. This equation establishes a relationship between purely mechanical and thermal phenomena (thermal conductivity) in a gas. The quantities in it are directly measured experimentally.

Table 10 gives data obtained in measuring the viscosity, coefficient of thermal conductivity, and the specific heat capacity of selected gases, as well as the values of the ratio $\lambda/\eta c_V$ calculated from these data, which according to Eq. (3.48) should equal unity.

*Table 10*

| Gas | $\eta \times 10^5$, kg/m·s | $\lambda \times 10^2$, W/m·K | $c_V$, J/kg·K | $\frac{\lambda}{\eta c_V}$ |
|---|---|---|---|---|
| Nitrogen | 1.66 | 2.36 | 745.2 | 1.91 |
| Oxygen | 1.92 | 2.39 | 653.0 | 1.91 |
| Water vapour | 1.21 | 2.40 | 1532.0 | 1.24 |
| Carbon dioxide | 1.38 | 1.42 | 632.1 | 1.63 |

A glance at Table 10 shows that as regards the order of magnitude of the relevant quantities Eq. (3.48) is obeyed quite well. A better coincidence of the results of experiments with the theoretical value of $\lambda/\eta c_V = 1$ can hardly be expected if we take into account the approximate nature of the calculations of the viscosity $\eta$ and the coefficient of thermal conductivity $\lambda$.

The viscosity or coefficient of internal friction should, like the coefficient of thermal conductivity, depend on the temperature because the expression for $\eta$ includes the mean velocity of thermal movements of the molecules, which depends on the temperature proportional to its square root. Hence, the viscosity should also grow with increasing temperature in proportion to $\sqrt{T}$.

Actually, the viscosity grows at a somewhat greater rate than in proportion to $\sqrt{T}$. The explanation is that an increase in the temperature is attended not only by a growth in the thermal velocity of the molecules, but also by diminishing of the effective cross section of the molecules. This causes the free path to grow, the distance from the site of the last collision before a given layer becomes greater and, therefore, the change in the impulse which a molecule brings along with it grows.

Thus, the molecular-kinetic ideas of the mechanism of viscosity set out here well agree with experimental results both qualitatively and quantitatively.

Since the expression for $\eta$ includes the mean free path, then measurement of the viscosity, like measurement of the thermal conductivity coefficient, permits us to determine (or at least to assess) the dimensions of molecules.

## 3.15. MEASUREMENT OF VISCOSITY (VISCOSIMETRY)

We have already mentioned that the viscosity can be determined by measuring the velocity of the flow of a gas through a tube or pipe having known geometrical dimensions. The viscosity can be calculated from the results of such measurements using the Poiseuille formula (3.45).

It must be borne in mind, however, that not any tube is suitable for such an experiment. The matter is that the flow of the gas must be *laminar* for measurement of the viscosity. This term denotes such a flow of a gas (or liquid) when the velocity of the gas in a direction at right angles to the axis of the tube equals zero at all points, i.e. when the separate layers of the gas flow parallel to one another, although they have different velocities. At a definite value of the flow velocity depending on the properties of the gas and the radius of the tube, however, eddies begin to appear in the gas that violate the laminar nature of the flow. The Poiseuille formula does not hold for such an eddy or *turbulent* flow. The smaller the cross section of the tube, the higher is the velocity needed for eddies to appear. To prevent the appearance of eddies at ordinary velocities, the tube must be very thin or, as we say, capillary.

Therefore the method of measuring the viscosity based on use of the Poiseuille formula is often called the capillary method, and the corresponding instruments are referred to as capillary *viscosimeters*.

We know from the mechanics of fluids (gases and liquids) that the transition from laminar to turbulent motion occurs, although not abruptly, but in quite definite conditions connected with the properties of the fluid, the dimensions of the tube, and the velocity. Thus, for a flow in a cylindrical tube, the transition to turbulent motion occurs when the dimensionless quantity

$$Re = \frac{\rho u r}{\eta} \tag{3.49}$$

becomes greater than a certain critical value of the order of magnitude of 1000. Here $\rho$ is the density of the gas, $u$ is the mean flow velocity, $r$ is the tube radius, and $\eta$ is the viscosity of the gas. This quantity is called the *Reynolds number*. When it is smaller than the critical value, motion is laminar; when it is greater, motion is turbulent.

The Reynolds number, generally speaking, characterizes the ratio between the inertial and viscosity forces acting in a fluid that is in motion. It also

has a simple molecular-kinetic meaning, however. Substituting for $\eta$ in Eq. (3.49) its value from Eq. (3.47), we get

$$Re \approx \frac{u}{\bar{v}} \frac{r}{l} \tag{3.50}$$

Hence, for the flow of a gas to become turbulent, either the velocity of the gas must be great in comparison with the mean velocity of thermal motion of the molecules, or the radius of the tube must be great in comparison with the free path. The second condition is virtually always complied with in a gas, the first almost never. This does not hinder the Reynolds number *Re* from having values higher than the critical one. For motion to be laminar, the velocity of a gas $u$ must be small. Only in this case can *Re* be lower than the critical value (about 1000).

**Method of Oscillation Damping.** To measure the viscosity, we do not need to have the gas flow without fail relative to the walls of a vessel at rest. We can also use the motion of a solid wall relative to the gas. This is how matters are in viscosimeters where the viscosity is determined according to the damping of the oscillations of a disk, sphere, or cylinder suspended in the gas being studied and performing oscillations in it. The principle of operation of such a viscosimeter will be clear from Fig. 61.

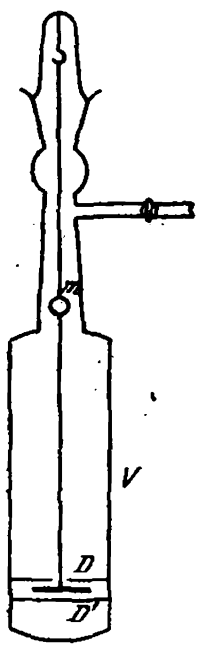


Fig. 61

Two disks $D$ and $D'$ are fastened in glass vessel $V$. The distance between the disks is a few millimetres (such small distances are needed to ensure a laminar flow). Another disk is suspended between them on a thin thread (this disk is of glass in the apparatus we are describing) and can perform torsional oscillations together with the suspending string. The string carries mirror $m$ which helps us to observe the oscillations of the disk. To induce the torsional oscillations, two small magnets with oppositely directed poles are fastened on the same string.

If the disk is brought into oscillating motion and then left to itself, the amplitude of the oscillations will gradually diminish owing to the viscosity of the gas filling the vessel, and at a faster rate, the greater is the viscosity of the gas. The rate of attenuation of the amplitude is characterized by the so-called *logarithmic decrement*. It equals the natural logarithm of the ratio between the amplitudes of two consecutive oscillations.

Measurement of the viscosity consists in inducing torsional vibrations of the disk by means of an external magnet, measuring the amplitudes of two consecutive oscillations (according to the reflection of the illuminated scale in the mirror), and also the duration of one full oscillation (it is vir-

tually independent of the amplitude). We use these data to calculate the viscosity by the formula

$$\eta = \frac{\Delta - \Delta'}{\tau C} \tag{3.51}$$

where $\Delta$ = logarithmic decrement of the disk
$\Delta'$ = logarithmic decrement of the suspension without the disk (but with the mirror and the magnets)
$\tau$ = duration of one full oscillation
$C$ = constant depending on the properties of the apparatus.

The constant $C$ has to be determined first by measuring the viscosity of a gas for which it is known in the viscosimeter and using Eq. (3.51) to find the value of $C$.

The above apparatus is suitable for measuring the viscosity at low temperatures and low pressures.

## 3.16. RELATIONSHIPS BETWEEN TRANSPORT COEFFICIENTS

In Sec. 3.14, we obtained a simple relationship [Eq. (3.48)] between the coefficients of thermal conductivity and the viscosity:

$$\lambda = \eta c_V$$

If we now compare Eqs. (3.47) and (3.19) for the viscosity and the diffusion coefficient, we easily see that they are related by the equation

$$D = \frac{\eta}{\rho}$$

We already know that the quantity $\eta/\rho$ is called the *kinematic viscosity*. Now we see that it has the same dimension as the diffusion coefficient and numerically equals it. This is not by chance because the kinematic viscosity does have the meaning of a certain diffusion coefficient. Indeed, the viscosity $\eta$ is an impulse flux (related to a unit velocity gradient). On the other hand, the product of the density of a gas $\rho$ and the velocity is the impulse of a unit volume. Therefore the ratio of the impulse flux $\eta$ to the density $\rho$ is the *velocity flux*. This gives us every right to call the kinematic viscosity the *velocity diffusion coefficient*.

Finally, if we compare Eqs. (3.19) and (3.39) for the coefficients of diffusion and thermal conductivity, we get

$$D = \frac{\lambda}{\rho c_V} \tag{3.52}$$

where $c_V$ is the specific heat capacity at constant volume. We have already encountered the quantity $\lambda/\rho c_V$ when considering the process of levelling out of the temperature (see p. 165) and called it the coefficient of temperature conductivity. It was indicated that this coefficient has the meaning of

the coefficient of temperature diffusion. This can easily be seen by analysing the right-hand side of Eq. (3.52). Indeed, the coefficient of thermal conductivity $\lambda$ determines the *flux* of the quantity of heat transported by a gas. The quantity $\rho c_V$, on the other hand, is the heat capacity of a unit volume of the gas. We know that the change in the temperature of a gas is determined by the ratio of the quantity of heat supplied to it to the heat capacity of the gas ($\Delta T = \Delta Q/C$). Therefore, the ratio of the *flux* of the quantity of heat to the *heat capacity*, i.e. $\lambda/\rho c_V$, is obviously the *flux* of the temperature at a temperature gradient equal to unity, i.e. the coefficient of temperature diffusion.

It follows from the above that the transport phenomena we have considered can be interpreted as processes of diffusion of a substance, the temperature, and the velocity, respectively. This is exactly what explains the above quantitative relationships between the transport coefficients $D$, $\lambda$, and $\eta$, which are well justified experimentally.

Any of the transport coefficients being measured experimentally permits us to assess the mean free path $l$ of a molecule and, therefore, the size of a molecule, as we did according to the measured value of the coefficient of thermal conductivity (see p. 168). The values of the cross sections of molecules of a given gas calculated from different transport coefficients coincide quite closely and are called *gas-kinetic* cross sections.

CHAPTER 4

# PHYSICAL PHENOMENA IN RAREFIED GASES (A VACUUM)

We have seen that a number of phenomena in gases, and first of all transport phenomena, are closely related to collisions between molecules. The quantitative characteristics of these phenomena therefore depend on the free path of the molecules.

In this connection, it is very interesting to study the properties of gases in conditions when there are no collisions between the molecules. It is quite simple to create such conditions because the free path of molecules is inversely proportional to the pressure of a gas:

$$l \propto \frac{1}{p}$$

At sufficiently low pressures, the free path of molecules may reach values exceeding the dimensions of the vessel containing the gas. For example at a pressure of about $10^{-6}$ mm Hg, which can easily be created by modern means for evacuating gases, the mean free path of molecules reaches several scores of metres (whereas at atmospheric pressure it is about $10^{-5}$ cm). With such a pressure in a vessel of conventional dimensions (several scores of centimetres), the molecules of a gas will virtually never collide with one another. Collisions will occur only with the walls of the vessel.

Such a rarefaction when the mean free path of molecules becomes greater than the dimensions of the vessel containing the gas is called a *vacuum*. The concept of a vacuum is therefore a relative one: the smaller the dimensions of the vessel containing a gas, the higher is the pressure at which the conditions of a vacuum are created in it. For example for a gas in a porous substance with a pore diameter of the order of magnitude of $10^{-5}$ cm, already atmospheric pressure is a vacuum, and some properties of such substances are explained by this circumstance.

Let us consider some phenomena that proceed appreciably differently in a vacuum than at high pressures. They include first of all transport phenomena — heat transfer, viscosity, and diffusion.

## 4.1. HEAT TRANSFER IN GASES AT LOW PRESSURES

It follows from Eq. (3.39) for the coefficient of thermal conductivity, i.e. $\lambda = \frac{1}{3} mn\bar{v}lc_V$, that this coefficient does not depend on the pressure because among the quantities in this equation only $n$ and $l$ do depend on it, and they are in the equation in the form of their product that is independent of the pressure. This corollary of the kinetic theory that has been well supported by experiments at conventional pressures stops being true in a gas at a low pressure (in a vacuum).

If the pressure of a gas has reached a value at which the mean free path of its molecules $l$ becomes greater than the dimensions of the vessel containing the gas, then the customary concept of thermal conductivity as a phenomenon due to collisions between molecules loses its meaning. This is the reason why we have used the term "heat transfer" here instead of thermal conductivity.

Heat is also transported (heat transfer) in a rarefied gas, but its mechanism is absolutely different. Since the molecules here collide only with the walls of the vessel, the process of heat transfer in a vacuum from a hotter surface to a colder one can be described approximately as follows. When molecules of a gas collide with the hotter surface, they acquire energy corresponding to the temperature of this surface. After rebounding from it, the molecules without colliding with one another reach the colder surface, transmit their surplus energy to it and rebound from it with an energy corresponding to the temperature of the cold wall. When heat is transferred from one surface to another in this way, there is no temperature gradient inside a gas, and therefore the concept of thermal conductivity loses its meaning.

It is evident that the quantity of heat transferred by a gas is proportional to the number of collisions of its molecules with the walls, i.e. to the pressure of the gas. This is what distinguishes a rarefied gas from a conventional, dense one.

Although we cannot speak about a temperature gradient in a vacuum, we can write by analogy with the Fourier equation (3.31) that

$$q = -\lambda \frac{T_1 - T_2}{d}$$

where the quantity $(T_1 - T_2)/d$ has been introduced instead of the gradient $dT/dx$ (here $T_1 - T_2$ is the difference between the temperatures of the walls,

and $d$ is the distance between them). Hence for the coefficient of "thermal conductivity", we can formally write the previous expression (3.39):

$$\lambda = \frac{1}{3} \rho \bar{v} l c_V$$

But here by the free path $l$ we must understand the distance $d$ so that

$$\lambda = \frac{1}{3} \rho \bar{v} d c_V \tag{4.1}$$

Substituting in Eq. (4.1) the quantity $mn$ for the density $\rho$, and the quantity $p/kT$ for $n$, we get

$$\lambda = \frac{1}{3} \frac{pm\bar{v}dc_V}{kT} \tag{4.2}$$

Finally, multiplying and dividing the right-hand side of Eq. (4.2) by the Avogadro constant $N_A$ and bearing in mind that $mN_A c_V = C_V$, and $kN_A = R$, we get

$$\lambda = \frac{1}{3} \frac{pd\bar{v}C_V}{RT} \tag{4.3}$$

Inspection of Eq. (4.3) shows that the coefficient of "thermal conductivity" of a gas is proportional to the pressure $p$. It must be borne in mind, however, that this coefficient does not characterize only the gas because it depends on the distance $d$ between the walls.

The dependence of heat transfer in a vacuum on the pressure explains, for example, why *Dewar vessels* (often called vacuum bottles in everyday life) are made with double walls the space between which is evacuated to the minimum possible pressure of the gas. These vessels, generally manufactured in the form of a cylinder or sphere (Fig. 62), are intended to isolate their contents from heat exchange with the surroundings. Dewar vessels, particularly, are used to store liquids boiling at low temperatures such as liquid air, liquid hydrogen, and liquid helium. Owing to the poor transfer of heat through the vacuum created between the walls of a Dewar vessel, the liquid in it receives little heat from the surroundings, and evaporates at a sufficiently slow rate. For the same reasons, a hot liquid in a Dewar vessel cools slowly because it gives up little heat to the surroundings.

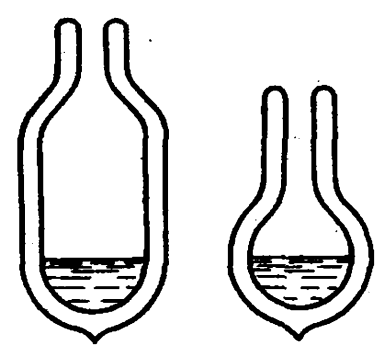


Fig. 62

As long as the pressure of the air between the walls of a Dewar vessel is such that the mean free path of the molecules is less than the distance between the walls, the transfer of heat through the air is determined by its

thermal conductivity and is virtually independent of the pressure. Although the thermal conductivity of gases is low, it is nevertheless too great to permit a Dewar vessel to play its part of a thermal insulator, and must be lowered by diminishing the pressure. With the conventional distances between the walls of a Dewar vessel (about 1 cm), a decrease of the pressure in the space between them to a value having the order of magnitude of $10^{-2}$ mm Hg does not yet result in lowering of the thermal conductivity in comparison with its value at atmospheric pressure. But upon a further decrease of the pressure, the heat transfer becomes proportional to the pressure, and when $p$ reaches a value of about $10^{-3}$ mm Hg, the heat transfer already becomes one-tenth of the value at atmospheric pressure. It continues to diminish with a further drop in the pressure.

## 4.2. FLOW OF GASES AT LOW PRESSURES (MOLECULAR FLOW)

The flow of gases in the conditions of a vacuum also occurs in a different way than at ordinary pressures.

The flow of a dense gas along a pipe or tube (at low velocities) depends on its viscosity. Particularly, the pressure difference needed to maintain this flow and balanced by the force of internal friction is proportional to the viscosity $\eta$ (Poiseuille's law). We have already learned that the viscosity itself is due to collisions between molecules, and therefore the viscosity or coefficient of internal friction is proportional to the free path of the molecules:

$$\eta = \frac{1}{3} mn\bar{v}l$$

Conditions are absolutely different in a vacuum when there are no collisions between the molecules. Friction is now connected with the transfer of the impulse directly to the walls because it is only with the latter that the molecules collide. We can therefore say that friction stops being "internal" and the concept of viscosity loses its previous meaning.

The flow of a gas in conditions when the molecules do not collide with one another is called *molecular flow*.

In the absence of collisions between molecules, the flow of a gas at first sight should not depend on the difference between the pressures in different portions of the gas. Indeed, a molecule freely flying from wall to wall is not acted upon by other molecules. Hence, its motion should not change as a result of the fact that the density of the molecules (their number in a unit volume) and, consequently, the pressure have changed in a portion of the gas.

Experiments have shown, however, that a pressure difference is also needed for a molecular flow. The explanation is that the molecular flow of a gas from one part of a vessel to another occurs exclusively owing to the chaotic nature of the molecular movements.

Imagine a vessel divided by a partition with an opening into two equal parts. And suppose that the vessel contains only one molecule. It is easy to understand that during a sufficiently long time our molecule will get into both parts of the vessel an equal number of times although there are no forces that would transfer it from one part of the vessel to the other.

If the vessel contains a lot of molecules, and they are originally all gathered in one half of it, with the passage of time the chaotic motion of the molecules will cause first one, then another of them to get into the other half of the vessel. During a sufficiently long time, all the molecules on an average will get into both halves of the vessel with the same frequency. The result will be that on an average each half of the vessel at each moment will contain the same number of molecules so that the pressure in all parts of the vessel will be the same. The levelling out of the pressure has been achieved, however, not by the action of forces, but by the chaotic nature of the molecules' movements.

It is not at all difficult to calculate the flow of a gas through such an opening in a partition separating two parts of a gas that are under different pressures if the latter correspond to the conditions of a vacuum. It is essential, however, that the dimensions of the opening be small in comparison with the free path of the molecules.

Let one part *I* of a gas at a pressure $p_1$ be separated from its other part *II* at a pressure $p_2$ by a partition with an opening (Fig. 63). The area of the latter is $A$. Assume for purposes of unambiguity that $p_1 > p_2$. Let us determine the quantity of the gas flowing through the opening in a unit time.

The number of molecules $N$ passing through a unit area of opening $AB$ in a unit time equals the difference between the numbers $N_1$ and $N_2$ of

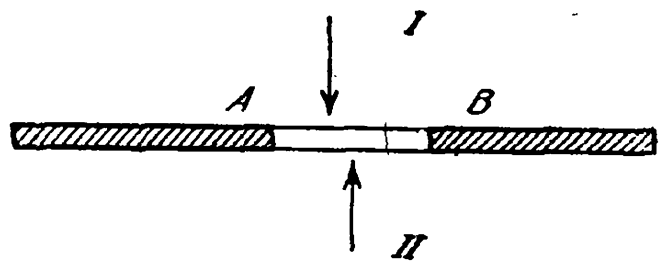



Fig. 63

molecules passing through this unit area in a unit time from directions *I* and *II*, respectively. If the density of the molecules (their number in a unit volume) in part *I* is $n_1$, then the number of molecules crossing a unit area in a unit time from the side of *I* is proportional to the product $n_1\bar{v}$, where $\bar{v}$ is the mean velocity of thermal motion of the molecules. Precise calculations give for $N_1$ the expression that we obtained on a previous page (see p. 78):

$$N_1 = \frac{1}{4} n_1 \bar{v} \tag{4.4}$$

In a vacuum, every molecule moves individually; its motion is not affected by the presence of other molecules. Therefore, the motion of the molecules from side *II* does not depend in any way on their motion in the opposite direction. Hence it follows that

$$N_2 = \frac{1}{4} n_2 \bar{v}$$

where $n_2$ is the density of the molecules in *II*. For the quantity $N$, we get

$$N = N_1 - N_2 = \frac{1}{4}(n_1 - n_2)\,\bar{v} \tag{4.5}$$

From Eq. (1.6), we get the following expression for the numbers of molecules per unit volume:

$$n_1 = \frac{p_1}{kT} \quad \text{and} \quad n_2 = \frac{p_2}{kT}$$

Substituting these values for $n_1$ and $n_2$ in Eq. (4.5), we get

$$N = \frac{1}{4}\bar{v}\frac{p_1 - p_2}{kT} = \frac{1}{4}\bar{v}\frac{\Delta p}{kT}$$

This is the number of molecules passing in one second through a unit area of the opening.

The number of molecules passing through the entire area $A$ of the opening in one second is

$$N' = NA = \frac{1}{4}\bar{v}\frac{\Delta p}{kT} A$$

The mass of the gas flowing through the opening in one second is

$$M = mN' = \frac{1}{4}\bar{v}\,\frac{m}{kT} A\,\Delta p \tag{4.6}$$

where $m$ is the mass of one molecule. Since $m = \mu/N_A$ (where $\mu$ is the molecular mass of the gas, and $N_A$ is the Avogadro constant), then

$$M = \frac{1}{4}\bar{v}\frac{\mu}{RT} A\,\Delta p \tag{4.7}$$

If the quantity of a gas flowing through the opening is expressed in moles per second ($Q$) instead of in grammes per second, we have

$$Q = \frac{M}{\mu} = \frac{1}{4}\bar{v}\frac{A}{RT}\Delta p$$

Substituting for $\bar{v}$ its value obtained after slight transformations from Eq. (1.58), i.e. $\bar{v} = \sqrt{\frac{8}{\pi}\frac{RT}{\mu}}$, we get

$$Q = \frac{1}{\sqrt{2\pi\mu RT}} A \Delta p \tag{4.8}$$

It is exactly these equations which determine the quantity of a gas that flows through a small opening in a diaphragm placed in a vacuum. The quantity of a dense gas flowing through an identical opening at the same pressure difference will be much greater.

The process of the flow of a gas through a small opening or orifice under the influence of a pressure difference is called *effusion* of the gas. Particularly, the flow of a gas through an opening in the conditions of a vacuum which we have just considered is called *molecular effusion* (or *Knudsen flow*).

## 4.3. MOLECULAR FLOW OF A GAS IN A CYLINDRICAL TUBE

The flow of gases along pipes or tubes (with low velocities) at ordinary pressures is described by the Poiseuille equation. According to it, the *volume* of a gas flowing in a unit time through a tube having a radius $r$ under the action of the pressure difference $p_1 - p_2 = \Delta p$ along the length $L$ of the tube is

$$V = \frac{\pi r^4}{8\eta}\frac{\Delta p}{L} \tag{4.9}$$

where $\eta$ is the viscosity of the gas.

For the *mass* of a gas $M$ flowing through a tube in a unit time, we get

$$M = \bar{\rho} V = \bar{\rho}\frac{\pi r^4}{8\eta}\frac{p_1 - p_2}{L} \tag{4.10}$$

Here $\bar{\rho}$ is the mean density of the gas in the tube equal to the half-sum of the densities at the pressures $p_1$ and $p_2$. The density of a gas $\bar{\rho}$ according to the equation of state of an ideal gas is

$$\bar{\rho} = \frac{M}{V} = \frac{(p_1 + p_2)\mu}{2RT} = \frac{\bar{p}\mu}{RT}$$

Using this value of $\bar{\rho}$ in Eq. (4.10), we get

$$M = \frac{\pi r^4 \mu}{16\eta RT}\frac{p_1^2 - p_2^2}{L} \tag{4.11}$$

This is the mass of a gas flowing in a unit time through a tube having the radius $r$ with viscous flow (the viscosity is $\eta$) at the temperature $T$.

The Poiseuille law expressed by Eqs. (4.9), (4.10), and (4.11) can be applied only to a dense gas when the free path of the molecules is small in comparison with the radius of the tube along which the gas flows. In this case, the flow of the gas may be considered as the flow of a continuous medium in which the molecular structure of the gas does not tell under the action of a pressure difference, and methods of hydrodynamics may be used. In the molecular flow of a gas when the free path of the molecules is greater than the cross-sectional dimension of the tube, the gas can no longer be considered as a continuous medium. On the contrary, in this case, the molecular structure of the gas manifests itself completely, and the equations given above may not be used.

Calculations which we have omitted here show that in the molecular flow of a gas through a tube (capillary) with the radius $r$ the quantity of a gas $Q$ (in moles) flowing in a unit time is determined by the formula

$$Q = \frac{2}{3} \frac{\bar{v}}{RT} \frac{r}{L} A \Delta p \tag{4.12}$$

where $A = \pi r^2$ = cross-sectional area of the tube
$\Delta p$ = pressure difference along the length $L$ of the tube.

From Eq. (1.58), as previously, we find that $\bar{v} = \sqrt{\frac{8}{\pi} \frac{RT}{\mu}}$. Using this value in Eq. (4.12), we get

$$Q = \frac{4}{3} \sqrt{\frac{2\pi}{\mu RT}} \frac{r^3}{L} \Delta p \tag{4.13}$$

or, after transformations,

$$Q = \frac{8\pi}{3} \frac{1}{\sqrt{2\pi\mu RT}} \frac{r^3}{L} \Delta p \tag{4.14}$$

Correspondingly, the mass of a gas flowing through a tube (in kg/s) is

$$M = \frac{8\pi}{3} \sqrt{\frac{\mu}{2\pi RT}} \frac{r^3}{L} \Delta p \tag{4.15}$$

Equations (4.15) and (4.14) are similar to Eqs. (4.7) and (4.8) for molecular effusion with the only difference that instead of the orifice (opening) area $A$ they include the quantity $8\pi r^3/3L$ also having the dimension of area.

Unlike the Poiseuille equation for a viscous flow, *the quantity of a gas flowing through a cylindrical tube in conditions of a vacuum is proportional to the third power of the tube radius* instead of the fourth.

As should be expected, in molecular flow through a tube at a given pressure difference, as in molecular effusion, the quantity of a gas [Eq. (4.12)] flowing in a unit time depends only on the thermal velocity of the molecules

and on the geometrical dimensions of the tube. It does not depend, however, on the viscosity of the gas.

At first sight, the law of molecular flow leads us to the paradoxical conclusion that the mass of a gas flowing through a tube in a unit time depends only on the pressure difference (with given dimensions of the tube, a definite temperature, and for a given gas) at the inlet and outlet of the tube, but does not depend on the values of the pressures $p_1$ and $p_2$ themselves. This means, for instance, that the mass of a gas flowing in one second through an opening or a capillary 0.1 mm in diameter does not depend on whether the pressures at the ends of the tube (or at both sides of the opening) are 0.015 and 0.014 mm Hg or 0.002 and 0.001 mm Hg, although the mean density of the gas in the first case is ten times greater than in the second (the free path of the molecules at a pressure of 0.015 mm Hg is about 0.5 cm, i.e. considerably greater than the diameter of the capillary).

The explanation is that when the pressure simultaneously increases at both sides of an opening (or at both ends of a capillary), the number of molecules migrating in both directions grows. In the absence of collisions, these counterflows of molecules do not affect each other, and the difference between these flows, which is what determines the quantity of a gas flowing through the capillary, remains constant and independent of the pressure. For dense gases, on the other hand, the mass of the gas flowing through a capillary at the given pressure difference is proportional to the mean pressure of the gas $(p_1 + p_2)/2$, as follows from the Poiseuille law (4.11).

Equations (4.11) and (4.15) have been verified by numerous experiments, each conducted for its own region of pressures. Approximate empirical equations describing the flow of a gas have been found for intermediate pressure regions.

Equations (4.11) and (4.15) are used in calculations of the geometrical dimensions (diameter and length) of pipes or tubes intended for the passage of a gas with a given velocity, for example for evacuating a gas from a vessel. A glance at these equations shows how greatly the rate of evacuation depends on the diameter of the pipe connecting the vessel being evacuated to the pump. If the diameter of the pipe has not been selected correctly (it is too small), it may happen that the quantity of a gas which the pipe can let through is less than that which can be handled by the pump. In this case, the capacity of the pump cannot be utilized completely.

## 4.4. MOLECULAR FLOW OF A MIXTURE OF GASES. SEPARATION OF GAS MIXTURES

The distinctive features of the molecular flow of gases through openings or capillaries are used to separate gas mixtures.

It was shown above that both in molecular flow along tubes or pipes and in molecular effusion the quantity of gas flowing through a cross section

in a unit time is inversely proportional to the square root of the molecular mass of the gas:

$$Q \propto \frac{1}{\sqrt{\mu}}$$

The lighter a gas, the greater is the flow of the gas, other conditions being equal. Hence it follows that if we pass a *mixture* of gases differing from one another in their molecular mass and, therefore, in the thermal velocities of their molecules through a system of openings or capillaries, the molecular flow of the lighter component of the mixture will be greater than that of the heavier one. As a result, the composition of the mixture will change at the outlet from the openings or capillaries: the concentration of the light component in the mixture will be greater than its concentration at the inlet. The mixture will become richer in the light component.

It is not difficult to calculate the degree of separation of a mixture upon its molecular flow through an opening or a capillary. We have already indicated in Sec. 3.10 that the degree of enrichment of a mixture is customarily characterized by the *enrichment factor* $a$. We shall remind the reader once more how it is determined.

Let the concentration of the light component in the initial mixture of two gases be $c_1$. Hence, the concentration of the heavy component is $1 - c_1$, and the relative concentration of the light component will be $c_1/(1 - c_1)$.

As a result of flowing of the gas through openings or capillaries, the concentration of the light component at their outlet will grow to a certain value $c_0$, the concentration of the heavy component will correspondingly become equal to $1 - c_0$, and the relative concentration of the light component will now be $c_0/(1 - c_0)$.

This relative concentration is obviously greater than the initial one, i.e

$$q = \frac{c_0}{1 - c_0} \Big/ \frac{c_1}{1 - c_1} > 1 \tag{4.16}$$

This ratio would equal unity if there were no enrichment.

We called the deviation of the ratio of the relative concentrations from unity the enrichment factor $\varepsilon$ (see Sec. 3.10). This means that

$$\frac{c_0}{1 - c_0} = \frac{c_1}{1 - c_1}(1 + \varepsilon) \tag{4.17}$$

If the molecular masses of the two components differ only slightly from each other, as is the case, for example, with isotopes, then the enrichment factor is very small, i.e. $\varepsilon \ll 1$. In this case, Eq. (4.17) can be simplified and written as follows:

$$c_0 - c_1 = \varepsilon c_0(1 - c_0) \tag{4.18}$$

Let us calculate the value of the enrichment factor $\varepsilon$.

Consider two volumes of a gas separated by a system of openings (or capillaries) $D$ (Fig. 64).

The initial gas mixture having a concentration of the light component of $c_1$ flows in at point $A_1$ under a pressure of $p_1$. A small portion of the

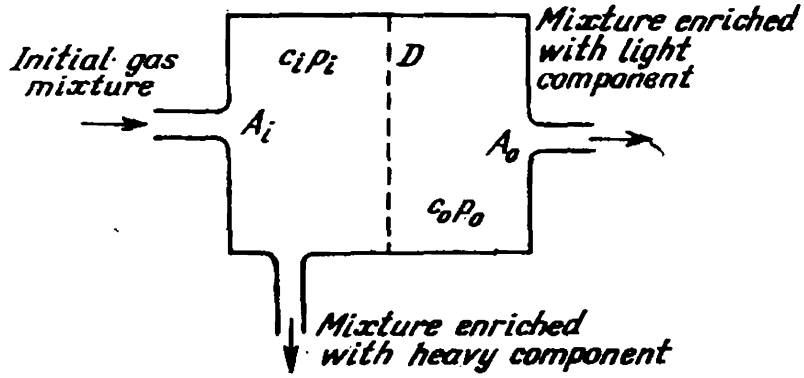



Fig. 64

mixture further passes through the system of openings $D$ and after becoming rich in the light component emerges through $A_0$ under a pressure of $p_0$. The remaining portion is drained off (see Fig. 64). Assume that $p_1 > p_0$ and $p_1 - p_0 = \Delta p$.

The dimensions of the openings are such that the flow of the gas through them is molecular, i.e. within the confines of the area of the openings the molecules do not collide with one another, and, consequently, each component of the mixture travels independently of the other one. Let $p_{1,1}$, $p_{1,h}$, $p_{0,1}$, and $p_{0,h}$ stand for the partial pressures of the light and the heavy components at the inlet and outlet, respectively. This means that

$$p_{1,1} = c_1 p_1, \quad p_{1,h} = (1 - c_1)p_1, \quad p_{0,1} = c_0 p_0, \quad p_{0,h} = (1 - c_0)p_0$$

Denoting the molecular masses of the light and heavy components of the mixture by $\mu_1$ and $\mu_h$, respectively, we get the following expression for the flow of the light component $Q_1$ through the openings [according to Eqs. (4.8) and (4.13)]:

$$Q_1 = \frac{C}{\sqrt{\mu_1}}(p_1 - p_{0,1}) = \frac{C}{\sqrt{\mu_1}}(c_1 p_1 - c_0 p_0) \tag{4.19}$$

and for the flow of the heavy component

$$Q_h = \frac{C}{\sqrt{\mu_h}}(p_h - p_{0,h}) = \frac{C}{\sqrt{\mu_h}}[(1 - c_1)p_1 - (1 - c_0)p_0] \tag{4.20}$$

where for an opening

$$C = \frac{A}{\sqrt{2\pi RT}} \tag{4.21}$$

and for a capillary

$$C = \frac{8\pi}{3} \frac{1}{\sqrt{2\pi RT}} \frac{r^3}{L} \tag{4.22}$$

Let $K$ stand for the ratio $p_0/p_1$ (the value of $K$ is less than unity), hence

$$Q_1 = \frac{C}{\sqrt{\mu_1}} p_1(c_1 - Kc_0), \qquad Q_h = \frac{C}{\sqrt{\mu_h}} p_1[(1 - c_1) - (1 - c_0)K]$$

Further, it is obvious that $Q_1/Q_h = c_0/(1 - c_0)$ and, therefore,

$$\frac{c_0}{1 - c_0} = \sqrt{\frac{\mu_h}{\mu_1}} \frac{c_1 - Kc_0}{1 - c_1 - K(1 - c_0)} \tag{4.23}$$

After simple transformations, we get the change in the concentration of the mixture we are interested in:

$$c_0 - c_1 = \frac{(\sqrt{\mu_h/\mu_1} - 1)(1 - K)(1 - c_0)c_0}{1 + (\sqrt{\mu_h/\mu_1} - 1)(1 - c_0)} \tag{4.24}$$

Inspection of this equation shows that the change in the concentration (enrichment) of a mixture of gases in molecular effusion through openings or capillaries grows with the increasing ratio $\mu_h/\mu_1$, i.e. with an increasing difference between the molecular masses of the two components of the mixture.

The above method has acquired special significance in connection with the problem of separating isotopes that differ only in their masses and cannot be separated by conventional chemical procedures. The use of the difference in the velocities of molecular flow of isotope atoms for their separation was found to be more effective than many other methods.

The relative difference between the molecular masses for mixtures of isotopes is usually quite insignificant (except for such light elements as hydrogen and helium) so that the ratio $\mu_h/\mu_1$ is close to unity. In this case, Eq. (4.24) becomes much simpler. If we denote the difference $\mu_h - \mu_1$ by $\Delta\mu$, then

$$\sqrt{\frac{\mu_h}{\mu_1}} = \sqrt{1 + \frac{\Delta\mu}{\mu}}$$

where $\mu = (\mu_1 + \mu_h)/2$ is the mean molecular mass of the mixture. Since the relative difference between the molecular masses $\Delta\mu/\mu$ is low for isotopes ($\Delta\mu/\mu \ll 1$), then limiting ourselves to the first two terms of the binomial series $(1 + \Delta\mu/\mu)^{1/2}$, we get

$$\sqrt{\frac{\mu_h}{\mu_1}} = 1 + \frac{1}{2} \frac{\Delta\mu}{\mu}$$

Substituting this value for $\sqrt{\mu_h/\mu_l}$ in Eq. (4.24), we get

$$c_0 - c_i = \frac{\frac{\Delta\mu}{2\mu}(1 - K)c_0(1 - c_0)}{1 + \frac{\Delta\mu}{2\mu}(1 - c_0)} \tag{4.25}$$

The second term in the denominator of this equation may be disregarded in comparison with unity because $\Delta\mu/2\mu \ll 1$. Hence,

$$c_0 - c_i = \frac{\Delta\mu}{2\mu} c_0(1 - c_0)(1 - K) \tag{4.26}$$

Now, using Eqs. (4.18) and (4.26), we can obtain an expression for the enrichment factor:

$$\varepsilon = \frac{c_0 - c_i}{c_0(1 - c_0)} = \frac{\Delta\mu}{2\mu}(1 - K) \tag{4.27}$$

As it was to be expected, the enrichment factor grows with an increasing relative difference of the molecular masses $\Delta\mu/2\mu$ of the components of an isotope mixture, and with an increasing ratio of the pressures $p_i/p_0 = 1/K$ causing effusion. Hence, to maintain a continuous separation process, we need a pump that would maintain the required ratio of the pressures or, as is said, the pressure drop under whose action the gas flows through the partition.

The method of molecular effusion was successfully used during the last decades to separate a considerable number of isotope mixtures of elements that are gases or form gaseous compounds. The isotopes of neon (Ne) were separated in this way. The gaseous carbon compound $CH_4$ (methane) was used to separate the carbon isotope with an atomic mass of 13 from the main isotope $C^{12}$.

The compound $UF_6$ — uranium hexafluoride — having a considerable vapour pressure was used in exactly the same way to separate the uranium isotopes with atomic masses of 235 and 238 ($U^{235}$ and $U^{238}$).

We have already indicated that the relative difference of the molecular or atomic masses $\Delta\mu/\mu$ for most isotopes is a small quantity. Hence, the enrichment factor $\varepsilon$ is also small so that effusion gives only a very small change in the concentration of the relevant isotope. Therefore, the molecular flow process is repeated many times in order to considerably enrich the mixture with one of the isotopes. Such a sequential repetition of the enrichment process carried out continuously introduces great complications into the practical use of the method notwithstanding the simplicity of the enrichment process itself. Nevertheless, this method has been considerably developed in the industry.

The above method of enrichment is often incorrectly called the diffusion method, whereas it ought to be called the *effusion* method. Diffusion is known to occur at the expense of a difference in the concentrations of the components on condition that the pressure of the gas is the same throughout the volume.

## 4.5. DIFFUSION OF GASES IN A VACUUM

Diffusion in gases is known to occur owing to the thermal movements of the molecules, and if it were determined only by the velocity of these movements, it would proceed almost instantaneously. Only the frequent collisions between molecules make diffusion a quite slow process.

In a vacuum when there are no collisions between the molecules, the diffusion of gases, i.e. the penetration of one gas into another, is indeed determined by the thermal velocity of the molecules, and here it is no longer a slow process. The molecules are not constricted by collisions and penetrate freely into any part of a vessel. Hence, diffusion occurs very rapidly.

Apart from the thermal velocities of the molecules, diffusion is affected by the shape and dimensions of the vessel which it occurs in. If diffusion takes place in a cylindrical vessel, the coefficient of diffusion (more exactly, the coefficient of self-diffusion) is determined by the following formula:

$$D = \frac{1}{3} \bar{v} d$$

where $\bar{v}$ = mean velocity of the molecules
$d$ = diameter of the vessel (tube).

This formula differs from the expression for the coefficient of diffusion of a dense gas in that it includes the diameter of the cylindrical vessel or tube instead of the free path. In the conditions of a vacuum, however, the distance between the walls of a vessel can be considered as the free path because it is exactly the walls that the particles collide with.

**Unsteady-State Diffusion.** The following experiment illustrates the process of diffusion in the conditions of a vacuum. Although in this experiment the diffusing gases are under atmospheric pressure, the conditions of a vacuum are nevertheless ensured by the gas diffusing through a porous substance in which the sizes of the pores are less than the free path at atmospheric pressure. Vessel $V$ (Fig. 65) made of a porous substance (for example of unbaked porcelain) is connected to manometer $M$. The vessel is placed in a glass filled with hydrogen (glass $G$ is turned over to prevent the hydrogen from volatilizing). The pressure in vessel $V$, which before this was naturally filled with atmospheric air, immediately begins to rise. This is detected according to the difference between the levels of the liquid in both limbs of manometer $M$. After the pressure in vessel $V$ has reached a certain maximum value, it begins to drop and finally reaches its initial value. If we then remove the glass with hydrogen, the pressure in vessel $V$ drops to below atmospheric, now reaches a certain minimum value, and

then after some time again rises to its initial value. All this is simply explained by the difference in the velocity of thermal movements of hydrogen and air molecules.

Indeed, at the beginning, when pure air was inside vessel $V$ and hydrogen was outside of it (in glass $G$), the hydrogen molecules penetrated into $V$ with a greater velocity than the molecules of air diffused from $V$ to $G$. Consequently, the pressure in vessel $V$ increased. Under the action of the appearing difference in pressures, the mixture begins to flow out, and the pressure levels out.

After the glass with hydrogen has been removed, vessel $V$ is again surrounded with atmospheric air, whereas inside it is a mixture of air and hydrogen. The hydrogen molecules, being the lighter ones, again diffuse through the porous walls of vessel $V$, but now outward. The pressure inside the vessel drops because the counterdiffusion of air into $V$ proceeds at a slower rate.

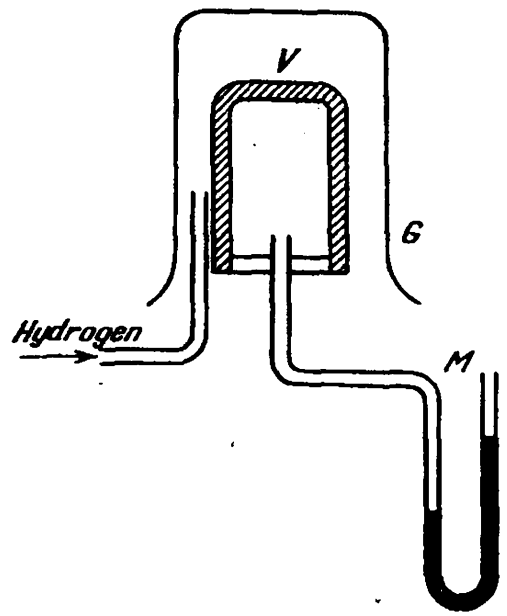


Fig. 65

The above experiment is an example of *unsteady-state diffusion* because the concentration of the diffusing gas continuously changes. But it gives a very clear idea of the mechanism of diffusion.

## 4.6. PRESSURE DIFFERENCE BETWEEN PARTS OF A GAS HEATED DIFFERENTLY (THERMAL TRANSPIRATION)

The absence of collisions between molecules in a rarefied gas results in a distinctive condition of equilibrium between different parts of a gas in a closed space.

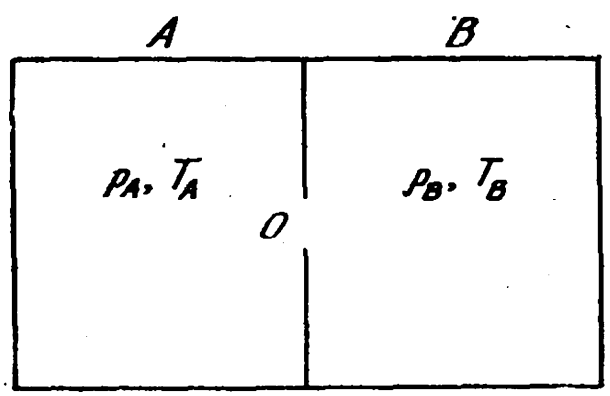


Fig. 66

Assume that two parts $A$ and $B$ of a vessel with a gas whose temperatures are $T_A$ and $T_B$, respectively, communicate with each other via opening $O$ (Fig. 66). In what conditions will equilibrium set in between parts $A$ and $B$,

i.e. will there be no motion of the gas? Equilibrium will evidently set in when the number of molecules passing from $A$ to $B$ equals the number of molecules travelling in the opposite direction during the same time, for example in one second.

The number of particles passing in one second through opening $O$ is proportional to the product of the number of particles in a unit volume and their thermal velocity. Hence, the condition of equilibrium of the gas can be written in the form

$$n_A \bar{v}_A = n_B \bar{v}_B \tag{4.28}$$

where $n_A$, $\bar{v}_A$, $n_B$, and $\bar{v}_B$ are the densities and the mean thermal velocities of the gas molecules in $A$ and in $B$, respectively. Taking into consideration that

$$n_A = \frac{p_A}{kT_A} \quad \text{and} \quad n_B = \frac{p_B}{kT_B}$$

we get the condition of equilibrium:

$$\frac{p_A}{\sqrt{T_A}} = \frac{p_B}{\sqrt{T_B}} \tag{4.29}$$

i.e. the pressures in both parts of the gas are proportional to the square root of the temperatures of these parts. For dense gases, a condition of equilibrium is the equality of the pressures in all parts of the gas:

$$p_A = p_B$$

Such a difference in the conditions of equilibrium seems strange at first sight because Eq. (4.28) contains nothing that would relate exclusively to a rarefied gas; it also holds for a dense gas. But at ordinary pressures, collisions of molecules result in motion of the gas as a whole, and this motion leads to levelling out of the pressures. In a rarefied gas, however, the molecules travel independently of one another, and a difference in temperatures cannot result in motion of the entire gas.

This is why the Pascal law is also violated in a rarefied gas. This law relates to the case when a gas behaves like an ordinary liquid, i.e. like a continuous medium. But at low pressures, the molecular structure of a gas tells in full measure, and it can no longer be considered as a continuous medium.

Experiments actually do confirm Eq. (4.29).

The first experiments involving the observation of the difference in pressures between two differently heated parts of a vessel containing a gas and divided by a partition with small openings (small in comparison with the mean free path of the molecules) were conducted by O. Reynolds (1879). He called this phenomenon *thermal transpiration*. His experiment is shown schematically in Fig. 67.

Plate $P$ of a porous substance (instead of an opening) is fixed in place between two ebonite rings covered with metal disks $D_1$ and $D_2$. The gas being studied (air) is confined in the space between these disks and the porous partition. Disk $D_2$ is cooled by running water, and disk $D_1$ is heated by steam, as shown in Fig. 67. A temperature difference is thus created between the parts of the gas at both sides of the porous plate. Pressure gauges connected via tubes $T_1$ and $T_2$ to the two parts of the vessel were used to measure the pressures $p_1$ and $p_2$.

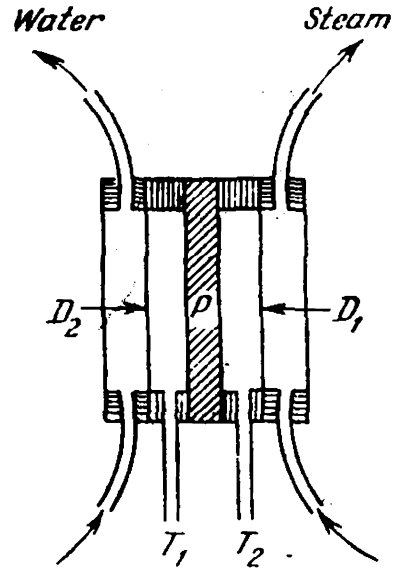


Fig. 67

Measurements showed that at sufficiently low pressures Eq. (4.29) is obeyed quite satisfactorily. At high pressures, the difference between the pressures in both parts of the vessel vanished.

The above phenomenon of thermal transpiration is of great significance when measuring the pressure in a vacuum if the pressure gauge or manometer which is naturally at room temperature is connected to the space being studied via a narrow duct (tube) whereas the space itself is at a temperature differing from room temperature. For example, in the parts of an apparatus that are at the temperature of liquid nitrogen (77 K), the pressure will be only 0.55 of that measured by a pressure gauge at room temperature. On the other hand, the pressure in a vessel heated in a furnace to 2000 kelvins will be almost three times higher than the reading of a pressure gauge connected to this vessel.

## 4.7. ELEMENTS OF VACUUM TECHNIQUE

The obtaining of low pressures (a high vacuum) in a vessel requires specific procedures and, accordingly, special equipment. Many processes in physics and engineering proceeding in the conditions of a very high vacuum have lately come to the forefront. Equipment has been developed for creating and maintaining such a vacuum, and instruments have been designed for measuring very low pressures of a gas.

Modern pumping equipment makes it possible to reach pressures of about $10^{-13}$ mm Hg. At such a pressure, the density of the molecules (their number in a unit volume) is about

$$n \approx \frac{3 \times 10^{19}}{760} \times 10^{-13} \approx 4000 \text{ cm}^{-3}$$

True, such a high vacuum can be obtained only in a small volume in an all-glass vessel from whose wall surfaces the absorbed gases have been removed by heating for a considerable time. A vacuum corresponding to a pressure of from $10^{-10}$ to $10^{-11}$ mm Hg has been successfully created,

however, in greater volumes of metal apparatuses which are liable to absorb gases to an even greater extent than glass.

A still higher vacuum can be created, naturally, in a way that is very simple in principle. For this purpose, the temperature of the vessel in which this vacuum is to be created must be lowered to a value of the order of magnitude of hundredths of a kelvin. At such a temperature, the vapour pressure of any substance is negligibly small. Even the vapour pressure of helium, which does not freeze at any temperature, is already lower than $10^{-30}$ mm Hg at this temperature. We can say that a complete vacuum has been created in a vessel in these conditions. But such a way of obtaining a high vacuum cannot have any practical significance owing to the intricate nature and high cost of the means for obtaining such low temperatures.

We shall now give a brief description of modern means for creating a high vacuum and methods of measuring low pressures used in science and engineering.

**Pumps.** Any device used to evacuate a gas from a confined space, i.e. to remove the gas molecules from it, is called a pump.

Pressures below $10^{-5}$ mm Hg are called a high vacuum. This is naturally a conditional boundary.

A vacuum pump must remove the gas from the vessel being evacuated and discharge it through the exhaust of the pump, overcoming the external pressure. The latter is therefore called the *counterpressure*. The higher the vacuum (i.e. the lower the pressure) that is needed, the lower should be the counterpressure at the pump exhaust.

No pumps exist that could evacuate a gas to a pressure of the order of magnitude of from $10^{-5}$ to $10^{-6}$ mm Hg (or lower) and discharge the exhausted gas into the atmosphere, i.e. with a counterpressure of 760 mm Hg. Hence, pumps creating a preliminary rarefaction are used to ensure a sufficiently low counterpressure. These pumps are usually called *fore* or *high-pressure vacuum pumps*. They are connected in series with the pump creating the required high vacuum — a high-vacuum or low-pressure vacuum pump.

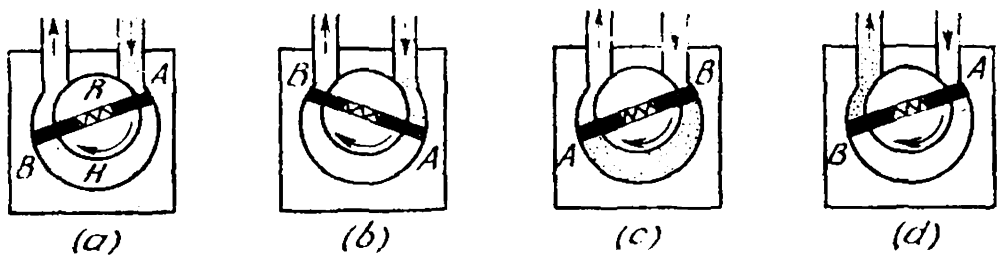



Fig. 68

The fore pump operates directly against atmospheric pressure.

**Fore Pumps.** In addition to the names "fore pumps" and "high-pressure vacuum pumps" mentioned above, these pumps are also often called *backing*, *roughing* or *preevacuation pumps*. Among the diverse kinds of fore pumps in use, rotary oil pumps of various designs are in the greatest favour. The design of such a pump and its operating principle are shown in Fig. 68.

Steel cylinder (rotor) *R* lubricated with oil revolves in cylindrical housing *H* provided with an inlet and an outlet pipes. The centres of the housing and the rotor do not coincide. The rotor revolves so that it constantly tightly fits against the inner surface of the housing at its upper part. Two flat plate blades *A* and *B* are arranged in the diametral plane of the rotor. A spring between the blades forces them apart and tightly presses them against the inner surface of the housing. The housing space is thereby divided into two or three parts depending on the position of the rotor during its revolution. When the blades are in the position shown in Fig. 68*b*, a portion of the gas from the space being evacuated enters the housing through the inlet pipe. Next, this portion is separated from the inlet pipe (in the position shown in Fig. 68*c*) as a result of turning of the rotor, and upon further motion of the latter it is compressed by blade *B* and is forced out via an exhaust valve in the outlet pipe (see Fig. 68*d*). Next a new portion of the gas flows into the housing from the space being evacuated, and so on. It is easy to see that the gas is removed from the crescent-shaped space by the blades twice during one revolution of the rotor. Such a pump can be used to achieve a pressure as low as 0.05 mm Hg at its inlet.

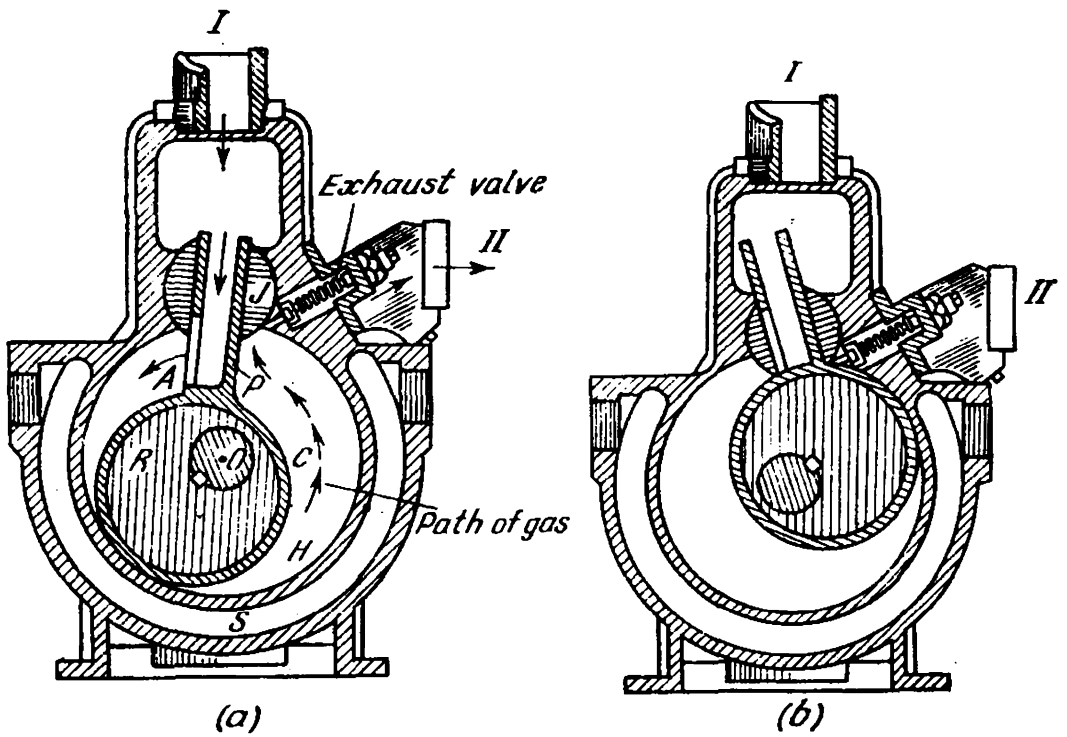



Fig. 69

Another design of a fore pump is shown in Fig. 69. Here rotor *R* in the form of an eccentric revolves about an axis passing through centre *O* of housing *H*, but not through the centre of the rotor. It is arranged inside casing *C* provided with flat hollow plate *P* having aperture *A* in its broad part. It is exactly the casing that functions as a piston forcing out the air or gas through the outlet pipe. Plate *P* passes through joint *J* permitting it to incline to both sides from its vertical position. Upon turning

of the rotor, casing *C* is in constant contact with the inner surface of the housing and together with plate *P* divides the housing space into two or three parts.

Figure 69*a* shows the pump in the position when the air is being sucked in from the space to be evacuated via inlet pipe *I*, and Fig. 69*b* in the position when the air is being forced out via outlet pipe *II*. During operation, the pump is cooled by running water flowing through space *S* surrounding the housing.

**High-Vacuum Pumps.** Unlike the mechanical fore pumps described above, modern high-vacuum pumps have no moving mechanical components. Their operation is based on the entrainment of the molecules of the gas being evacuated by a jet of vapour of a liquid, generally mercury or oil. This is why these pumps are called *vapour-jet pumps*. They are frequently also called *diffusion pumps* because their operation is connected with diffusion of the particles of the gas being evacuated into the jet of vapour.

High-vacuum pumps of this kind can function only with a sufficiently low counterpressure, the latter being ensured by a fore pump. A diffusion pump is therefore connected in series with a fore pump so that the exhaust of the diffusion pump is connected to the inlet of the fore pump.

The design of a steam-oil diffusion pump, which at present is the most widespread kind, is shown schematically in Fig. 70. Evaporating liquid *L* is at the bottom of vessel *V*, usually made of metal. Evaporation of the liquid is ensured by electric heater *H*. The space being evacuated is connected to upper end *A* of the pump, and the inlet pipe of a fore pump to its outlet pipe *B*. After the fore pump has created the required pressure in the pump and the space being evacuated, the heater is switched on, and the liquid

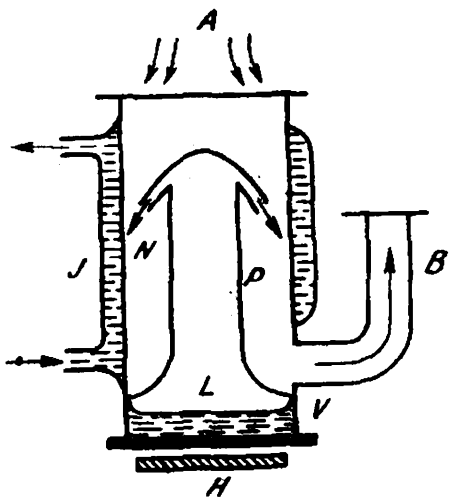



Fig. 70

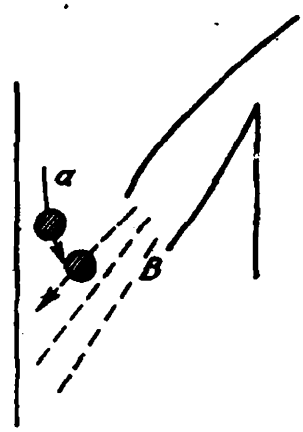



Fig. 71

begins to intensely evaporate. The vapour rises along pipe *P* placed above the liquid, is discharged with a high velocity from nozzle *N* which pipe *P* terminates in, and then condenses on the walls and flows down to the bottom of the vessel. The walls of the vessel are surrounded by "jacket" *J* inside

which water circulates. Thus the heater and cooler of the pump ensure continuous circulation of the vapour.

The molecules of the gas being evacuated flowing in from region *A* are entrained by the jet of vapour discharged from the nozzle, are carried to the lower part of the pump where they get into outlet pipe *B* and are discharged by the fore pump to the atmosphere.

The main purpose of the vapour jet is to transmit part of its impulse (momentum) to the molecules of the gas being evacuated and direct them downward to the outlet pipe. The pressure of the gas at the exhaust of a high-vacuum pump is obviously equal to the pressure created by the fore pump, i.e. to about $10^{-2}$ mm Hg.

The lowest pressure to which the vessel connected to *A* can be evacuated is mainly determined by the vapour pressure of the working liquid at the temperature of the cooling water above the nozzle. Therefore, such grades of oil are chosen as the working liquid of high-vacuum pumps that have a low vapour pressure at room temperature.

Let us consider in somewhat greater detail the mechanism of functioning of a vapour-jet (steam-jet) pump.

Figure 71 is an enlarged view of a part of nozzle *N* and the adjoining cooled wall of the pump housing.

The pressure in the space being evacuated before the beginning of pump operation is already low enough for the free path of the molecules to be compatible with the dimensions of inlet pipe *A* (see Fig. 70) connecting the pump to the space being evacuated. This means that the molecules of the gas do not virtually collide with one another. At any rate, the molecules collide with the walls more often than with one another. In these conditions, the only reason why a molecule, for instance molecule *a* (Fig. 71), gets into the pump is the chance coincidence of the direction of the velocity of this molecule with a vertically downward direction, i.e. from region *A* to vapour jet *B*. In other words, the gas being evacuated diffuses from the vessel containing it toward the vapour jet (this is why pumps of this kind are called diffusion ones). If a collision of molecule *a* with a vapour molecule results in its getting into the jet, it can virtually no longer return because the vapour pressure in the jet is sufficiently high, reaching values of up to 10 mm Hg. At such a pressure, back diffusion of the molecules of the gas may be left out of consideration. And this means that the gas molecules are "entrained" by the jet.

Some molecules of the gas upon collision with the vapour molecules may naturally acquire a velocity directed away from the jet. But this does not mean that they will not be pumped out because one of the following collisions will impart the required direction of motion to them.

The circumstance that some molecules when colliding with the vapour molecules acquire a velocity directed back to the inlet pipe only slows up somewhat the rate of evacuation. Operation of the pump is determined not by these comparatively rare cases, but by the circumstance that the mole-

cules which have diffused into the jet can virtually no longer return. And since the rate of diffusion in a vacuum is known to be very great, then vapour-jet pumps have a quite appreciable rate of evacuation.

The molecules entrained by the jet of vapour are either directly discharged by it toward the forevacuum or collide with the wall on which the vapour condenses. Upon this condensation, the gas carried along by the jet is liberated and is also removed by the fore pump.

Vapour-jet pumps usually have not one, but several nozzles (usually two or three) that function consecutively (multi-stage pumps).

Modern diffusion pumps can evacuate vessels to a pressure having the order of magnitude of from $10^{-9}$ to $10^{-11}$ mm Hg, and in certain conditions still lower. But such a high vacuum can be obtained provided that the entire vacuum system is completely airtight. It is also essential that the surfaces of the vessel being evacuated and of other parts of the vacuum system liberate no gases. It is very difficult to ensure both these conditions, especially the second one, in practice. The matter is that a greater or smaller amount of gases is always liberated from the surface of virtually any bodies. These gases were either adsorbed on the surface or dissolved inside the body. With a high vacuum, it is sufficient for a very small amount of the gases to be liberated and the pressure will change appreciably even in a considerable volume.

**Sorption of a Gas (Getters).** A number of substances are able to absorb or, as is said, sorb considerable amounts of gases. A typical example of such sorbents is carbon (or charcoal) whose ability of absorbing heavy gases was taken advantage of long ago in gas masks. The ability of carbon to absorb gases is mainly determined by its very developed surface due to its porous structure. To create a greater surface, the carbon is subjected to special treatment (activation). The sorption properties of carbon are especially great at low temperatures. This property is used to evacuate gases and to maintain the high vacuum that has already been achieved.

Some substances are capable of absorbing quite definite gases owing to the fact that they react chemically with them and form solid compounds. An example is titanium (Ti) which can absorb large amounts of hydrogen. This property of titanium is taken advantage of in a number of arrangements where it is necessary to evacuate hydrogen. Gas-absorbing substances are sometimes called *getters*.

## 4.8. MEASUREMENT OF LOW PRESSURES

A number of methods have been developed for measuring low pressures. Some of them will be described below.

It should be noted that there are no instruments for measuring low pressures that would be suitable within the entire range of pressures covered by the concept of a vacuum, just like there are no instruments capable of measuring any high pressures. We shall describe here the main instruments

(manometers) used in high-vacuum technique, beginning with the lowest pressures.

**Ionization Manometer.** Its design differs only slightly from that of conventional three-electrode amplifying valves. Its operating principle is based on ionization of a definite part of the molecules or atoms of the gas whose pressure is to be measured, i.e. their conversion into positively charged ions. An external electric field causes an ionic current to appear whose intensity is measured with the relevant instrument (a galvanometer).

If the power of the ionizer is constant, the intensity of the ionic current $i$ is proportional to the density of the ions (their number in a unit volume); the latter is known to be proportional to the pressure of the gas $p$. We can therefore write that

$$i = Cp$$

After finding the value of the proportionality factor $C$ by a special experiment, we acquire the possibility of determining the pressure of a gas according to the measured current $i$.

In ionization manometers, the gas is ionized by electrons when they collide with molecules (atoms) of the gas. This ionization is conducted in a three-electrode valve (triode) connected to the space being evacuated in which the pressure is being measured. The ionization manometer is connected as shown in Fig. 72.

The electrons ionizing the gas filling the triode (its pressure naturally equals that being measured) are emitted by the filament that is the cathode. The filament current is maintained by battery $B_1$ and is controlled by rheostat $R$.

The electrons emitted by cathode $C$ are accelerated by the electric field between the cathode and grid $Gr$ whose potential, as shown in Fig. 72, is kept positive relative to the cathode with the aid of e.m.f. source $B_2$.

The electrons that have passed through the grid ionize the gas in the space between the grid and collector $C_1$ whose potential is kept negative relative to the grid by source $B_3$. Therefore, the positive ions formed upon ionization of the gas migrate toward the collector and create an ionic current. The electrons, on the other hand, return to the grid. The intensity of the ionic current $i$ is measured by galvanometer $G$.

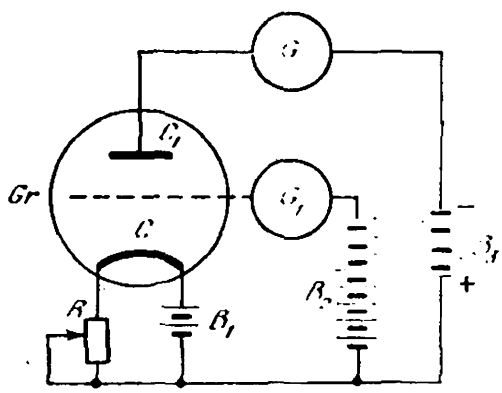


Fig. 72

For the intensity of the ionic current to be proportional to the pressure of the gas, the intensity of the electronic current (i.e. the power of the ionizer) must be kept constant. The constancy of this current is controlled with the aid of galvanometer $G_1$.

An ionization manometer must be graduated, i.e. the factor $C$ relating the intensity of the ionic current to the pressure of the gas must be deter-

mined. For this purpose, the intensity of the ionic current should be measured at several known values of the pressure determined with the aid of another manometer (for instance a McLeod manometer).

A shortcoming of an ionization manometer is the dependence of its readings on the composition of the gas (the factor $C$ differs for different gases). An ionization manometer can be used to measure pressures from $10^{-3}$ to $10^{-12}$ mm Hg.

**Thermal-Conduction Manometer.** Pressures ranging from 0.1 to $10^{-3}$ mm Hg are generally measured with a manometer whose operation is based on the pressure dependence of the thermal conductivity of a gas.

At very low pressures (in a high vacuum), the coefficient of thermal conductivity of a gas, as we have learned, is proportional to the pressure. In the region of pressures from 0.1 to 0.001 mm Hg, the coefficient of thermal conductivity already noticeably changes with the pressure, although not strictly proportional to the latter. This factor is what is used in the manometers of the kind being described. One of the manometers of this kind in the greatest favour is the thermal-conduction manometer, shown schematically in Fig. 73.

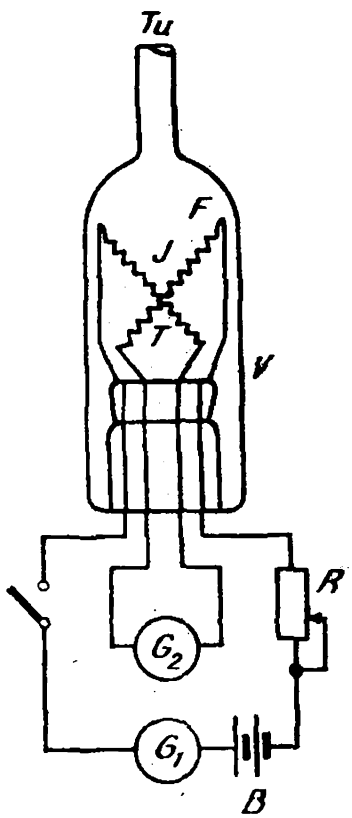


Fig. 73

Glass (or sometimes metal) vessel $V$ connected by tube $Tu$ to the space being evacuated contains thermocouple $T$. Its junction $J$ is heated by the electric current flowing along metal filament $F$ (heater) from source $B$. The heater is in direct proximity to the junction of the thermocouple. The current in the heater is kept constant with the aid of rheostat $R$ and is controlled by galvanometer $G_1$. Owing to heating of the junction of the thermocouple, a thermoelectromotive force (thermo-e.m.f.) appears across its ends, which is measured by galvanometer $G_2$.

The value of the thermo-e.m.f. is directly related to the pressure of the gas. Indeed, at a given current intensity in the heater, the temperature of the thermocouple junction that determines the magnitude of the thermo-e.m.f. being measured will be the higher, the lower is the transfer of heat from the junction to outside. The temperature of the junction becomes constant, i.e. equilibrium sets in when the power liberated by the heater equals the power transferred to outside through the gas. The heat transfer to outside is the greater, the higher is the thermal conductivity of the gas, i.e. the higher is the pressure. Hence it follows that the magnitude of the thermo-e.m.f. measured by the instrument grows with a decreasing pressure of the gas.

A thermal-conduction manometer is supplied together with a graduating curve — a curve showing the dependence of the thermo-e.m.f. being measured on the pressure of the gas. Sometimes not only a scale of the thermo-e.m.f., but also a pressure scale (the latter is not uniform) is marked on the scale of the measuring instrument itself.

Figures 72 and 73 show schematically how ionization and thermal-conduction manometers are connected. Galvanic batteries are shown as the sources of current in these diagrams. Actually, modern manometers are fed from a-c mains, and rectifiers and transformers are used instead of the relevant batteries. They are installed together with the other components in one box.

**McLeod Manometer.** This is one of the first manometers used for measuring very low pressures which was in great favour at one time and is still used quite often to date. The operating principle of a McLeod manometer is very simple and consists in the following.

A conventional U-tube mercury manometer cannot be used to measure too low pressures owing to the difficulty of reading small differences in the levels of the mercury in the manometer limbs. Therefore, to measure a low pressure of a gas, a quite definite previously known volume of the gas is taken and subjected to compression such that it will already be easy to measure the pressure of the gas according to the difference between the levels in the mercury manometer. The degree of compression of the separated portion of the gas must naturally be known. It is exactly this idea that underlies the design of a McLeod manometer, shown schematically in Fig. 74.

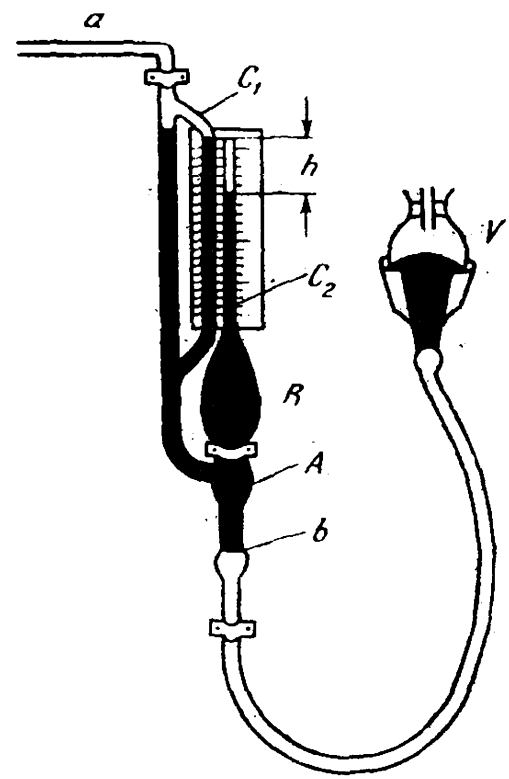


Fig. 74

Glass reservoir $R$ of a known volume with capillary $C_2$ soldered to it communicates via tube $a$ with the space being evacuated in which the pressure is being measured. Capillary $C_1$ having the same bore as capillary $C_2$ is soldered on parallel to the latter. Thus, capillary $C_1$ is always connected to the space being evacuated, and $C_2$ to reservoir $R$. The latter is connected by means of extension $b$ and a flexible hose to open vessel $V$ filled with mercury.

Before measurement, vessel $V$ is at such a height that the mercury in the left limb does not rise above point $A$. The difference between the levels in vessel $V$ and the left limb is about 760 mm. Reservoir $R$ at this time communicates with the space being evacuated. To measure the pressure,

vessel $V$ with mercury is lifted and thus reservoir $R$ is disconnected from the space being evacuated. Upon further lifting of the mercury, the gas in reservoir $R$ is compressed and forced into capillary $C_2$. The mercury is lifted until its level in capillary $C_1$ becomes equal to that of the upper end of capillary $C_2$. Next the difference is measured between the levels $h$ in the capillaries $C_2$ (the compressed portion of the gas is above this level) and $C_1$ (this capillary communicates with the space containing the gas whose pressure is being measured). The difference between the levels in the capillaries is measured in this position. It obviously equals the pressure of the compressed gas.

Using Boyle's law, it is simple to determine the pressure $p$ being measured (in mm Hg), i.e. the initial pressure in reservoir $R$ before the gas in it was compressed. Indeed, if the volume of reservoir $R$ is $V$, then

$$pV = hV_1$$

where $V_1$ is the volume of the gas compressed in capillary $C_2$:

$$V_1 = \pi r^2 h$$

here $r$ is the radius of the capillary. Hence,

$$p = \frac{hV_1}{V} = \frac{\pi r^2 h^2}{V}$$

The radius of the capillary $r$ and the volume of the reservoir $V$ are determined beforehand, and, therefore, the ratio $\pi r^2/V$ is a constant characterizing a given manometer. Measurement of the pressure, consequently, consists in measuring the difference $h$ between the levels in the capillaries. This simple procedure can be used to measure pressures ranging from 0.1 to $10^{-6}$ mm Hg.

McLeod manometers have the following shortcomings:

1. They do not measure the pressure of saturated vapour that may be present in the vacuum system; this vapour upon compression condenses and does not change its pressure.
2. The mercury vapour that fills the manometers is harmful for the health.
3. They do not allow the pressure to be controlled continuously.
4. They cannot be used to measure pressures lower than $10^{-6}$ mm Hg.

## 4.9. VACUUM SYSTEM

Figure 75 shows the layout of a typical vacuum system used to obtain a high vacuum.

Fore pump $P_f$ is connected to high-vacuum pump $P_v$ through a flexible hose with cock $c_1$. Sometimes a prevacuum vessel having a large volume is inserted in the line between the pumps. When such a vessel is used, the

system can operate with the fore pump disconnected — the gas being evacuated is discharged from the high-vacuum part not directly into the atmosphere, but into this vessel. Branch $B_1$ is used to connect a low-vacuum manometer (a U-tube mercury or thermal-conduction manometer). The high-vacuum pump is adjoined by a trap cooled with liquid air for freezing

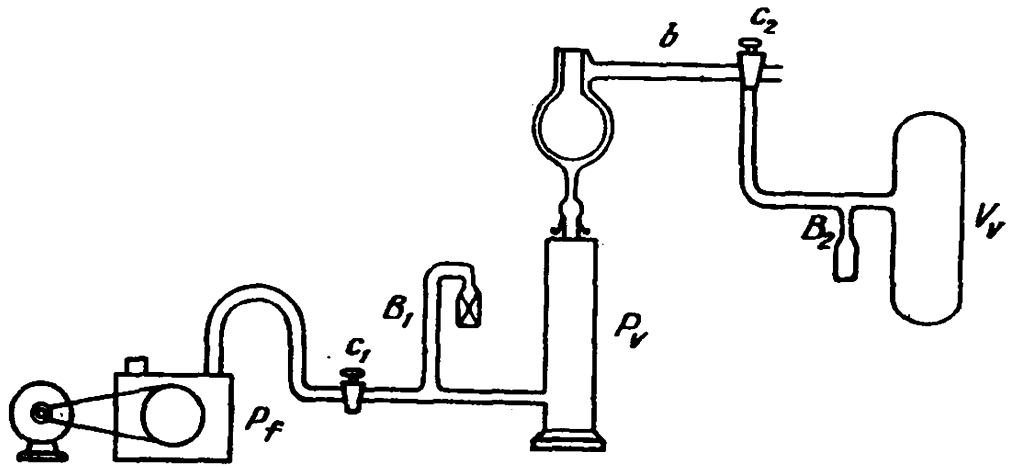



Fig. 75

out any vapour of the working liquid that may penetrate into the high-vacuum region. Such a trap is needed especially when the working liquid in pump $P_v$ is mercury. Tube $b$ via cock $c_2$ leads to vessel $V_v$ in which a high vacuum is to be created. Branch $B_2$ in this tube is used to connect a high-vacuum manometer — a McLeod or ionization one. Cock $c_2$ should preferably be a three-way one to provide the possibility of connecting the space being evacuated to the atmosphere when the high-vacuum pump is operating.

Vacuum systems may also have other layouts depending on their purpose.

CHAPTER 5

# REAL GASES. VAN DER WAALS EQUATION

We showed in the previous chapters that the Clapeyron equation sufficiently well describes the properties of gases known from experiments. But is this equation indeed accurate and true in all conditions, or does it correspond to the relationships observed experimentally only with a definite approximation?

When studying natural phenomena, physicists use experimental data — measurements — to establish quantitative relationships between the quantities characterizing the phenomenon being studied. These relationships are often approximate. This means that they hold only as long as the values of the quantities in them are within definite limits. Outside of these limits, they are no longer true, and more general relationships must be sought that are suitable for broader ranges of the values of the quantities we are interested in. It is very important to indicate the limits within which a given physical law may be applied because application of the law beyond the sphere of its applicability often leads to major errors.

Very few physical laws have a universal nature, i.e. are always true. Among them, for example, are the laws of conservation of energy and of momentum (for closed systems). These laws and their corollaries are fully accurate ones knowing no exceptions. But such a law as that of liquid friction is an approximate one — the force of liquid friction is proportional to the velocity of relative motion only at low velocities. At high velocities, the relationship between the force of friction and the velocity becomes more complicated.

## 5.1. DEVIATIONS OF GAS PROPERTIES FROM IDEAL GAS LAWS

The Clapeyron equation is also an approximate one. It holds only for sufficiently low pressures, and the lower the pressure, the more accurately is it observed. An increase in the pressure is attended by deviations from

such gas laws as Boyle's and Gay-Lussac's laws, which are direct corollaries of Clapeyron's equation of state.

Table 11 gives experimentally obtained values of the volume $V$ occupied by one mole of nitrogen $N_2$ at various pressures $p$ and a temperature of 0 °C, and values of the product $pV$.

*Table 11*

**Volume of 1 Mole of Nitrogen at Various Pressures**

| $p$, atm | $V \times 10^4$, m³ | $pV \times 10^4$, atm·m³ | $p$, atm | $V \times 10^4$, m³ | $pV \times 10^4$, atm·m³ |
|---|---|---|---|---|---|
| 1 | 224 | 224 | 700 | 0.532 | 372 |
| 100 | 2.4 | 240 | 900 | 0.483 | 437 |
| 300 | 0.85 | 255 | 1000 | 0.460 | 461 |
| 500 | 0.625 | 322 | | | |

Inspection of this table shows that already at a pressure of 100 atm the value of $V$ differs from the theoretical one by more than 7%. With a further increase in pressure, the values of the volume differ more and more from the ones theoretically calculated according to the Clapeyron equation, so that at a pressure of 1000 atm the volume of the gas is more than double the value it would have had if the Clapeyron equation were true. The same relates to the product $pV$, which according to the Clapeyron equation must remain constant at all pressures. Actually, it continuously grows with increasing pressure at high pressures, deviating more and more from the value required by the Clapeyron equation.

The above data show that at sufficiently high pressures a real gas is compressed by external forces to a considerably smaller degree than could be expected on the basis of the equation of state for an ideal gas. The compressibility of a gas diminishes with increasing pressure at a higher rate than inversely proportional to the pressure as is the rule for an ideal gas, for which in accordance with Eq. (1.14) we have

$$\varkappa = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{p}$$

At lower pressures, the relationship between the volume $V$ and pressure $p$ of a gas at constant temperature is more complicated. At comparatively low pressures, the curve expressing the relationship between the product $pV$ and the pressure $p$ for a given temperature (hence this curve is an isotherm) was found to have a minimum, i.e. at low pressures the quantity $pV$ diminishes with increasing pressure (the compressibility is greater than it should be for an ideal gas), at a certain pressure it reaches a minimum, after which it again begins to grow (the compressibility is smaller than that of an ideal gas).

The pressure at which the value of $pV$ passes through a minimum depends on the temperature.

There is a temperature that is characteristic for every gas (Boyle's temperature) at which the product $pV$ within a certain interval of pressures does not depend on the pressure, i.e. at this temperature the gas obeys Boyle's law.

Experiments thus show that real gases considerably differ in their properties from ideal ones. There is nothing surprising here if we remember the assumptions we made in deriving the equation of state for ideal gases. Indeed, we defined an ideal gas as one consisting of molecules that do not interact with one another, and we considered the molecules to be material points, i.e. we disregarded their dimensions and volume.

The absence of interaction between molecules means that no forces act on them in the intervals between collisions, i.e. that they travel freely. When molecules collide with one another, however, they change their velocity, which is impossible without the action of a force. Consequently, intermolecular forces do exist, but they become noticeable only upon collisions when the distances between the molecules are very small.

The notion of a molecule lacking volume implies that $V$ in the equation of state, i.e. the volume which the molecules move in, is completely available for the movement of each of them because all the other molecules, being points, occupy no volume. We rejected this assumption when considering the collisions of molecules, and we know that molecules do have definite dimensions. Experiments with transport phenomena give a value of the order of magnitude of $10^{-10}$ m for these dimensions.

Thus both assumptions on which the ideal gas theory is based are approximate. At atmospheric pressure, the mean distance between molecules is 10 times greater than their own dimensions while the volume occupied by a gas is 2000 times greater than the total volume of the molecules. In these conditions (and moreover at still lower pressures), we may ignore both the volume of the molecules and the forces of interaction between them if the latter rapidly diminish with an increasing distance between molecules. But already at a pressure of 100 atm, the distance between the molecules of a gas is on an average only double their own dimensions while the volume of the molecules themselves is only one-twentieth of the volume of the gas. In these conditions, the volume of the molecules may not be disregarded, and the forces of interaction should already tell not only at the moments of collisions.

## 5.2. LIQUEFACTION OF GASES (CONDENSATION)

The above failure of the experimental data on the pressure dependence of the volume of a gas to correspond to the equation of state for an ideal gas seems to be only of a quantitative nature. But important qualitative changes observed at sufficiently high pressures and the corresponding temperatures are also connected with it.

At definite values of the pressure and temperature, gases condense, i.e. pass over into the liquid state which appreciably differs from the gaseous one. This phenomenon does not follow at all from the equation of state for an ideal gas.

Let us consider this process in greater detail.

It can be investigated experimentally in the arrangement shown schematically in Fig. 76.

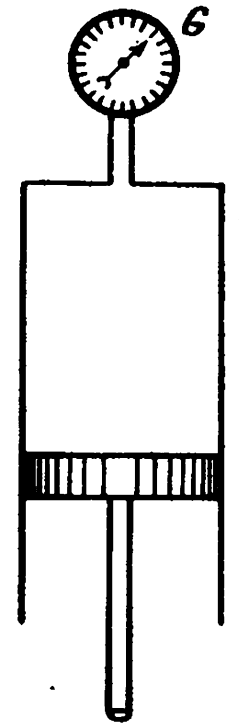


Fig. 76

Assume that the gas being investigated is placed in a vessel closed with a movable piston. We shall keep its temperature constant, but below a value characteristic for every gas. By moving the piston upward, we reduce the volume of the gas and increase its pressure, which is measured by pressure gauge *G*. As the piston is lifted and, consequently, the volume of the gas is reduced, its pressure continuously grows, first inversely proportional to the volume, and then slower and slower. Finally, the pressure reaches a certain maximum value and no longer grows, notwithstanding the fact that the lifting of the piston is continued. It can be noticed at exactly this moment that droplets of a liquid appear on the surface of the piston and the walls of the vessel.

Further upward motion of the piston is attended by an increase in the amount of the liquid above the piston and, accordingly, a reduction in the amount of the gas (vapour) over the liquid, but the pressure gauge shows a constant pressure. And it remains constant until the entire volume between the piston and the walls of the vessel is filled with the liquid. If we continue to lift the piston after this, i.e. compress the liquid, then even the most negligible reduction in the volume of the substance is achieved at the cost of a very great increase in the pressure. This means that the compressibility of the liquid is very small.

Instead of a piston whose motion compresses a gas, the liquid "piston" depicted in Fig. 77, showing a Cailletet press, is often used. The gas being studied is above a column of mercury that is moved by the action of an external pressure.

It is convenient to depict the above process of compression of a gas and its transformation into a liquid on a graph with the aid of an isotherm. We lay off the pressure measured by the pressure gauge along the axis of ordinates (Fig. 78), and the molar volume, i.e. the volume of one mole, along the axis of abscissas (we could lay off the specific volume, i.e. the volume of one gramme of the gas, with the same success). The graph in Fig. 78 illustrates what has been said above. At comparatively great specific volumes (a low density) of a gas, reduction of the volume is attended by an increase in the pressure (section *AB* of the curve). This continues until the volume diminishes to the value $V_1$. A further reduction of the

volume to the value $V_2$ does not cause the pressure to change. Beginning from $V_2$, a reduction in the volume now requires a sharp increase in the pressure.

At point $B$ corresponding to the volume $V_1$, the process of condensation begins, and by the moment when the volume reaches the value $V_2$ the entire

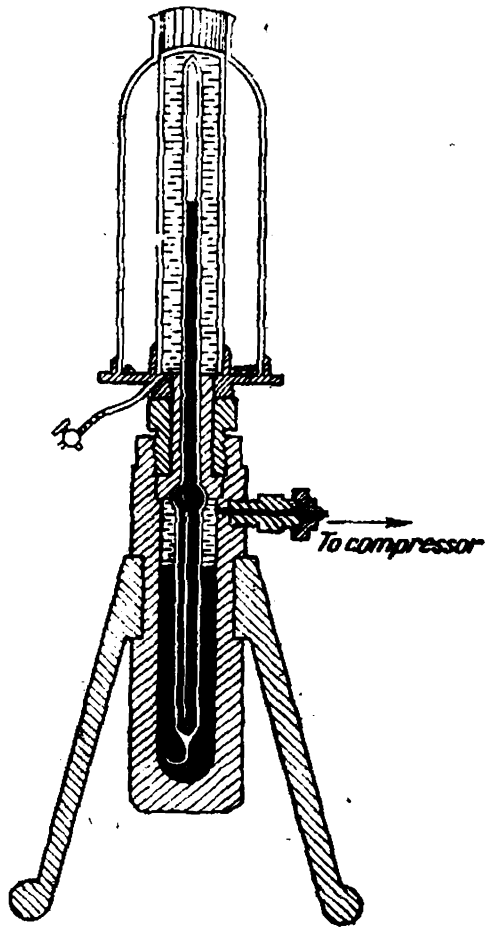



Fig. 77

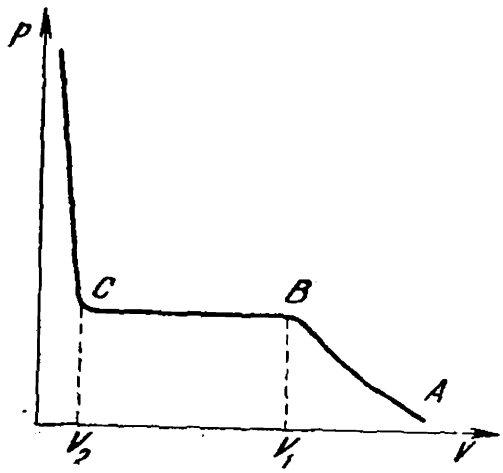



Fig. 78

gas transforms into the liquid state. Finally, a sharp increase in the pressure when the volume is diminished to below $V_2$ indicates that now the liquid itself is being compressed.

At the pressures and volumes corresponding to section $BC$, part of the volume of the vessel is occupied by the liquid and the other part by the gas, which in this case is called *saturated vapour*. The ordinate corresponding to section $BC$ determines the saturated vapour pressure at the given temperature.

To get a clearer notion of the quantities characterizing the process of condensation, we shall give certain numerical data relating to water (water vapour).

At 20 °C the pressure of saturated water vapour is 17.5 mm Hg. The molar volume of water vapour can be calculated with adequate accuracy from the equation of state for an ideal gas:

$$pV = RT;\ V = \frac{RT}{p} = \frac{8.31 \times 293}{17.5 \times 1.33 \times 10^2} = 1.04\ \text{m}^3/\text{mol}$$

The molar volume of the liquid (water) equals about $1.8 \times 10^{-5}$ m³. Hence, the ratio of the molar volumes of the vapour and the liquid $V_1/V_2$ is approximately 60 000. It is therefore impossible to depict an isotherm for 20 °C on a graph like that in Fig. 78 for water to the proper scale. The ratio $V_1/V_2$ diminishes at a higher temperature, but even for 100 °C, when the molar volume of the vapour $V_1$ already equals 3.1 m³/mol, it is nevertheless still 1700 times greater than $V_2$.

For still higher temperatures, the difference between $V_1$ and $V_2$ becomes still smaller. This means that the density of the saturated vapour $\mu/V_1$ grows with increasing temperature whereas the density of the liquid $\mu/V_2$ decreases.

Table 12 gives the values of the densities of water and saturated water vapour (steam) at different temperatures. A glance at the table shows that at a temperature of 647.25 K the densities of water and its saturated vapour become identical.

*Table 12*

**Densities of Water and Its Saturated Vapour (Steam) at Different Temperatures and Pressures**

| Temperature, K | Pressure, bar | Density of vapour, kg/m³ | Density of water, kg/m³ |
|---|---|---|---|
| 273.15 | 0.006 | 0.004 | 999.9 |
| 323.15 | 0.122 | 0.083 | 988.0 |
| 373.15 | 1.013 | 0.6 | 958.0 |
| 423.15 | 4.750 | 2.5 | 917.0 |
| 473.15 | 15.54 | 8.0 | 863.0 |
| 523.15 | 39.76 | 19.9 | 799.0 |
| 573.15 | 85.88 | 46.2 | 712.0 |
| 623.15 | 165.34 | 113.6 | 575.0 |
| 647.25 | 217.72 | 329.0 | 329.0 |

Consequently, at this temperature, the difference between the liquid and its saturated vapour vanishes. At temperatures above 647.25 K, water behaves like an ordinary gas, i.e. an increase in the pressure is attended by diminishing of the volume. Instead of two simultaneously existing states, a liquid and a gas, now only one state remains—a gas—although at a sufficiently high pressure the density of such a gas may become equal to that of a liquid and even exceed it.

All this naturally relates not only to water, but to any substance. There is a certain temperature for every substance at which the difference between the vapour and the liquid vanishes and above which the substance can be only homogeneous regardless of the compression it is subjected to. This temperature is called the *critical temperature*.

Different substances have different values of their critical temperature. We have seen that for water it equals 647.25 K. The critical temperature for nitrogen is 126.0 K, for oxygen 154.3 K, etc. The lowest critical temperature in nature is that of the rare helium isotope $He^3$ — helium with an atomic mass of 3. It is 3.35 K, or −269.80 °C.

T. Andrews was the first to experimentally investigate the equation of state for carbon dioxide at high pressures. The isotherms he obtained are shown in Fig. 79. Each curve corresponds to a definite temperature.

Let us consider the isotherm corresponding to the temperature of 13.1 °C beginning with high specific volumes, i.e. from the right. We see that in this part of the curve an increase in the pressure causes an appreciable decrease in the volume (section *AB*) which, true, is less steep than it ought to be in accordance with the Clapeyron equation.

At a pressure of 49 atm, condensation of the carbon dioxide begins. As long as it continues, the pressure remains constant, but the volume of

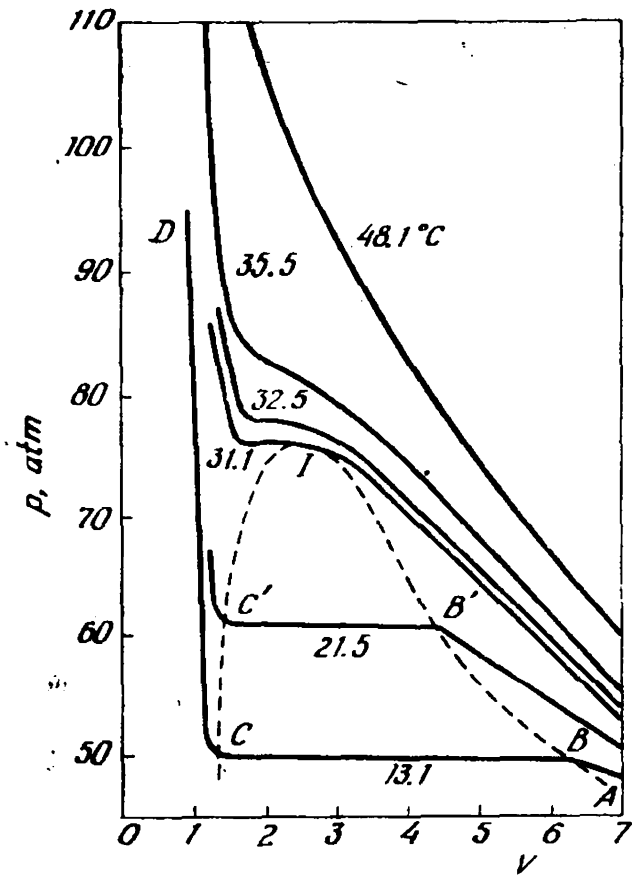



Fig. 79.

the gas diminishes as a result of transition to the liquid state. This corresponds to the horizontal section *BC* of the isotherm. At point *C*, the entire volume of the gas is condensed, after which the isotherm rises steeply. This means that now it is no longer gaseous carbon dioxide that is being

compressed, but liquid carbon dioxide whose compressibility $(1/V)(dV/dp)$ like that of any other liquid is very small.

The isotherms corresponding to higher temperatures have the same form, but like water, the ratio $V_1/V_2$ becomes smaller. This is expressed in the graph in that the horizontal section $BC$ becomes shorter and shorter: the

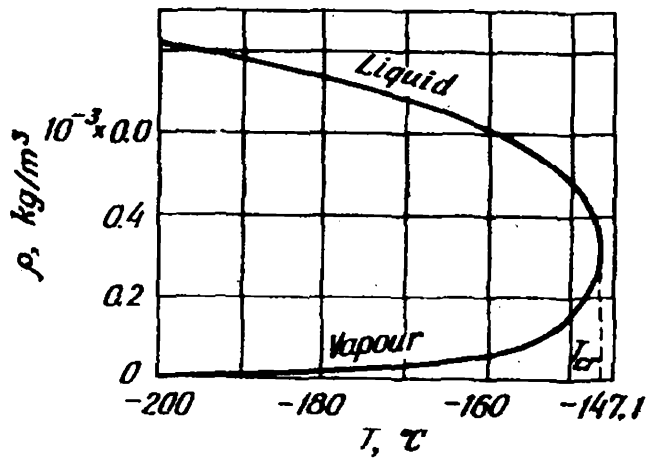



Fig. 80

specific volumes of the liquid and vapour approach each other because the former grows with increasing temperature and the latter diminishes. Finally, at a temperature of 31.1 °C (the critical temperature $T_{cr}$), the horizontal section of the curve disappears and gives way to a point of inflection $I$ — the specific volumes of the liquid and vapour (and, consequently, their densities) become the same. The isotherm itself corresponding to this temperature is called the *critical isotherm*.

At a temperature above critical, the formation of a liquid is no longer possible at any pressure. An increase in pressure results only in a reduction in volume (growth of the density). For a temperature above critical, for example for 48.1 °C (see Fig. 79), the isotherm of carbon dioxide has the same appearance qualitatively as an isotherm of an ideal gas.

A graph of a different kind can serve as another illustration of what has been said above. Figure 80 shows an experimentally obtained curve of the dependence of the density $\rho$ of liquid nitrogen and its saturated vapour on the temperature $T$. The curve shows how the density of liquid nitrogen diminishes with increasing temperature (the upper branch of the curve) while the density of its vapour grows (the lower branch) until at the critical temperature (−147.1 °C) both densities reach the same value. The corresponding specific (or molar) volume is called the *critical volume* ($V_{cr}$). The saturated vapour pressure at the critical temperature is called the *critical pressure* ($p_{cr}$). These three critical parameters — $p_{cr}$, $V_{cr}$, and $T_{cr}$ — determine the *critical state* of a substance.

Table 13 gives the critical parameters of selected substances.

*Table 13*

**Critical Parameters of Selected Substances**

| Substance | $T_{cr}$, K | $p_{cr}$, bar | $V_{cr} \times 10^3$, $m^3/kg$ | Substance | $T_{cr}$, K | $p_{cr}$, bar | $V_{cr} \times 10^3$, $m^3/kg$ |
|---|---|---|---|---|---|---|---|
| Helium ($He^3$) | 3.35 | 1.18 | — | Oxygen | 154.3 | 50.34 | 2.32 |
| Helium ($He^4$) | 5.25 | 2.29 | 14.43 | Methane | 190.6 | 46.39 | 6.17 |
| Hydrogen | 33.2 | 13.29 | 32.26 | Carbon dioxide | 304.2 | 73.94 | 2.17 |
| Neon | 44.3 | 26.23 | 2.06 | Ammonia | 405.6 | 112.94 | 4.26 |
| Nitrogen | 126.0 | 33.93 | 3.22 | Chlorine | 417.1 | 77.08 | 1.75 |
| Argon | 151.1 | 48.62 | 1.88 | Water | 647.25 | 220.53 | 2.50 |

## 5.3. PHASE TRANSITION

We have seen on the example of the phenomenon of gas condensation considered in the preceding section that two different states of the same substance can exist at the same temperature and pressure. These states differ in their properties, in the given case in their density.

In general, *if a system is divided into homogeneous and contiguous parts being in physically different states, these parts are called phases of the system.*

If two or more different phases of a substance at a given temperature and pressure exist simultaneously, being in contact with one another, and if the mass of one of the phases does not grow at the expense of the other, we have what is called *phase equilibrium.* The transition of a substance from one state (phase) to another is called a *phase transition.* The number of phases that can be in equilibrium may be different and depends on the composition of the substance.

Both the condensation of a gas and the reverse process — the transition of a liquid into a vapour (vaporization) are examples of phase transitions. We know that a substance can be in a third state — the solid one. The transition of a gas or liquid into the solid state is also a phase transition. But the difference of the solid state from a fluid one (this term is used to denote both the liquid and the gaseous states) is much deeper than that between the liquid and gaseous states. We shall consider the phase transition to the solid state on a later page.

Let us now return to the liquid-vapour (or vapour-liquid) phase transition.

If on the isotherms in Fig. 79 we connect the points of transition of the vapour into the liquid and the liquid into the vapour, i.e. points $B, B', \ldots,$

and $C$, $C'$, . . ., we get a smooth curve with a peak shown in Fig. 79 by a dash line and reproduced separately in Fig. 81.

Any point $R$ with the coordinates $p_0$ and $V_0$ to the right of branch $PZ$ of the curve obviously corresponds to the gaseous state because the specific volume $V_0$ is greater than the volume at which the transition to the liquid

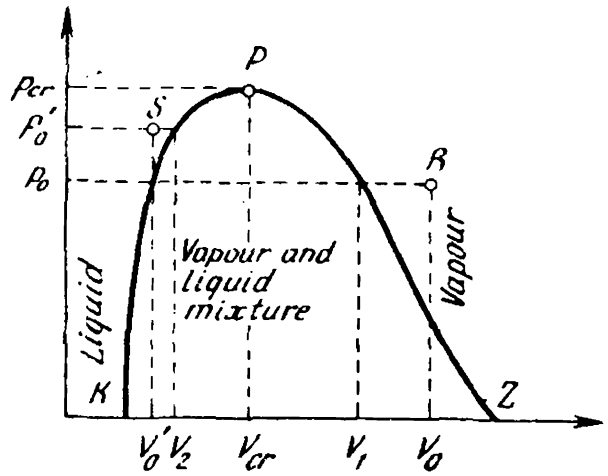



Fig. 81

state begins at the same pressure. Similarly, point $S$ with the coordinates $p_0'$ and $V_0'$, like any other point to the left of branch $PK$, corresponds to the liquid state—the specific volume $V_0'$ is less than the specific volume at which the process of condensation terminates. All the points inside of curve $KPZ$ correspond to two-phase states, i.e. to states at which the liquid and the saturated vapour over it exist simultaneously. Point $P$ corresponds to the critical state. Its coordinates on the curve in Fig. 81 are $p_{cr}$ and $V_{cr}$, i.e. the critical pressure and volume.

We have already learned that a substance can be transferred from the gaseous to the liquid state by increasing its pressure at the given temperature if the latter is below the critical value. Preliminary cooling is needed when the temperature is higher than $T_{cr}$. Upon such a transformation, the substance must pass through the intermediate region of a two-phase state when the vapour and liquid coexist and border with each other.

We can accomplish this transition, however, without passing through this region of two-phase states. In other words, we can convert a gas into a liquid (or vice versa) without both phases existing at the same time. For example, to transform a gas characterized by the volume $V_0$, pressure $p_0$, and temperature $T_0$ (see Fig. 81) into a liquid at the same temperature and pressure, but of course with another volume $V_0'$, we can proceed as follows. We heat the gas to a temperature above the critical value and then compress it so that its volume becomes equal to $V_0'$. Finally, while keeping the volume constant, we cool the gas to the temperature $T_0$. Its pressure

becomes equal to $p_0$. Thus, we can transform a gas into a liquid "bypassing" the region of two-phase states so that there will be no such intermediate state in which a border (meniscus) appears between a liquid and its vapour.

If, for example, we want to transform gaseous carbon dioxide at a temperature of 21.5 °C and a pressure of 50 atm into liquid carbon dioxide at the same temperature, we must first heat the gas to a temperature above 31.1 °C, for example to 32 °C. At this temperature, the gas must be compressed so that its specific volume becomes equal to 1.5 $m^3/g$. Its pressure will grow accordingly. After this, cooling to 21.5 °C will cause the entire gas to transform into the liquid state.

The possibility of a continuous transition from the gaseous to the liquid state without passing through the stage of the simultaneous existence of both phases shows that there is no qualitative difference of principle between them. The very fact of the existence of the critical state shows that in definite conditions the liquid and gaseous states cannot be distinguished. This is why we often speak of the continuous transition between them. The transition from the solid to the liquid or gaseous state cannot be accomplished in a similar way, i.e. so that at a certain temperature and pressure two phases of a substance would not exist simultaneously.

## 5.4. PHASE DIAGRAMS

As indicated above, equilibrium of the liquid and gaseous phases, i.e. equilibrium between a liquid and its saturated vapour, takes place at definite pressures and temperatures (below the critical temperature). A change in one of these quantities, for example the temperature, results in a change in the pressure at which phase equilibrium is possible, i.e. a change in the saturated vapour pressure. A glance at Fig. 79 shows that elevation of the temperature is attended by an increase in the saturated vapour pressure.

Figure 82 shows the temperature dependence of the saturated vapour pressure for water. For all other substances, this dependence is of the same nature.

Any point to the left of the curve corresponds to the liquid state, and points to the right of it correspond to the gaseous phase. This means that a vapour whose state is characterized by any point to the right of the curve will condense if its temperature is lowered while keeping the pressure constant*. In exactly the same way, a liquid whose state is given by the coordinates of any point to the left of the curve will transform into a vapour if its temperature is elevated. And only points on the curve itself correspond to phase equilibrium, i.e. to the simultaneous existence of a liquid and of a vapour above it.

*The vapour pressure can be kept constant, for instance, by letting a piston move freely over the vapour.

The curve in Fig. 82 that corresponds to equilibrium of phases is called a *phase diagram*, or a *curve of phase equilibrium* (in the given case of a liquid and a vapour). It separates regions whose points correspond to single-phase states of a substance and is one of the most important characteristics of

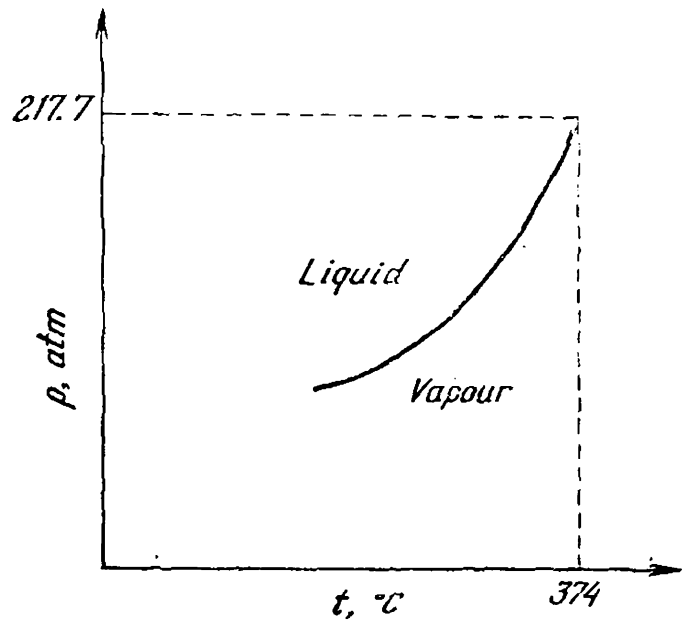



Fig. 82

a substance. A feature of the curve in Fig. 82 is that it has an end because it cannot be continued to above the critical temperature. Two phases do not exist above this temperature, and therefore there can be no equilibrium between them. We shall see below that the liquid-vapour equilibrium curve also has a beginning. An analytical expression for this equilibrium curve will be given in Chap. 7.

## 5.5. DETERMINATION OF THE CRITICAL PARAMETERS

It is easy to observe the process of the transition of a substance through the critical state in the following experiment. The liquid being studied (for example ether, with which it is especially convenient to conduct the experiment) is placed in a glass tube. After evacuation of the air from the tube, it is soldered (Fig. 83). The tube is then placed in a furnace provided with a mica window for observation. As the temperature rises, which is measured by a thermometer placed next to the tube, the meniscus — the interface between the liquid and its vapour — is watched.

At a definite temperature, the meniscus suddenly vanishes, and the tube is seen to be filled with a homogeneous substance. Vanishing of the visible interface shows that the densities of the substance at both sides of the previous border have become the same. Consequently, the temperature at

which the meniscus vanishes is the critical temperature. For ether, it equals 467.1 K. If we now cool the tube heated to a temperature above the critical one, at the same temperature of 467.1 K a mist consisting of droplets of a liquid will suddenly appear in the entire volume of the tube. These droplets rapidly fall to the bottom of the tube and form a layer of liquid which is again separated from the vapour by a sharp border — a meniscus.

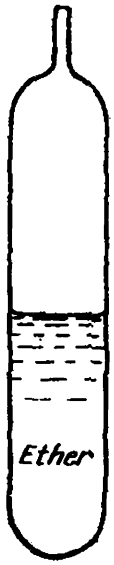


Fig. 83

It is thus easy to determine the critical temperature of a liquid by measuring the temperature at which a meniscus vanishes or appears in an airtight vessel with the liquid.

If the tube in the above experiment contains exactly the amount of liquid needed for its vapour to fill the entire volume of the tube when having the critical density, then the meniscus will not travel along the tube in heating. If the tube contains a greater amount of liquid, elevation of the temperature will be attended by upward motion of the meniscus until the entire tube is filled with the liquid. Conversely, if an insufficient amount of liquid is poured into the tube, the liquid will evaporate when heated, and the meniscus will move downward until the entire tube is filled with the vapour.

This is also clearly seen from the diagram in Fig. 81. In our experiment, unlike the ones described previously where the volume of the vessel changes when a piston moves, the volume of the substance always remains constant (the vessel is sealed). If the volume of the vessel is less than the critical one, i.e. the amount of the liquid is great, we shall always remain on the left-hand branch of the diagram which, as we know, corresponds to the liquid phase. Upon elevation of the temperature, the volume of the liquid phase grows as a result of condensation of the vapour, and the liquid fills the entire volume even before the critical temperature is reached because the critical volume is greater than the volume of the vessel. When the volume of a vessel is greater than the critical volume for the amount of substance placed in it, the state of the latter will correspond to the right-hand branch of the diagram (see Fig. 81). This means that, when heated, the volume of a liquid will diminish as a result of its evaporation.

Only when the volume of the tube (vessel) is exactly equal to the critical volume of the amount of substance in it, will elevation of the temperature result in no appreciable change in the volume of the liquid or vapour. Heating of the liquid causes its evaporation, and the result is a higher density of the vapour. But the volume of the liquid grows as a result of thermal expansion by about such an amount as to compensate for the reduction in its volume due to evaporation. This causes the density of the liquid to diminish until at the critical temperature it becomes equal to the density of the vapour above the liquid. Now the entire substance will be in the critical state when it no longer can be considered to be either a liquid or a gas.

The above considerations underly a simple way of determining the critical density and, consequently, the critical volume of a substance. It consists in the following.

Different amounts by weight of the liquid being studied are poured into small tubes (usually of quartz). It is seen that in all the tubes the liquid is in a *surplus* amount in comparison with that needed for the volume of the tube to be filled with the substance having its critical density at the critical temperature. After this, the tubes are soldered. Next they are heated, and the temperature is measured at which the meniscus reaches the top edge. Knowing the mass of the liquid in the tube and its volume, we determine the density of the liquid at the temperature at which it completely filled the tube. After performing such measurements for all the tubes containing different amounts of the liquid, we can plot a curve showing the temperature dependence of the liquid density. Extrapolation of this curve to the critical temperature (which we know, of course) gives us the density of the liquid being studied at the critical temperature. Knowing the density, we find it a simple matter to calculate the critical volume.

Similar experiments, but carried out with tubes containing different amounts of the liquid by weight *not sufficient* for obtaining the critical state, also make it possible to obtain the density of the vapour at the critical temperature and, consequently, the critical volume of the substance.

Both series of experiments should give the same result because the densities of the liquid and vapour equal each other at the critical temperature.

## 5.6. VAN DER WAALS EQUATION

The features of the behaviour of a gas at increased pressures and the gas-liquid phase transition are not described by the Clapeyron equation which holds only for gases at low pressures (ideal gases). It is possible, however, to improve this equation so that it will not only correctly describe the properties of real gases at any pressures, but will also describe, with a certain approximation, the properties of liquids and the phase transition from the gaseous to the liquid state.

For this purpose, it is evidently essential to give up our notion of gas molecules as material points deprived of dimensions and our assumption that there are no forces of interaction between molecules. If it is assumed that intermolecular forces do exist and that molecules have a definite size, and if the corresponding corrections are introduced into the Clapeyron equation, there is hope of obtaining a new equation of state for real gases that will better agree with experimental facts.

Such an improved equation of state that takes into account both the finite size of the molecules and the forces of interaction between them was proposed in 1873 by J. van der Waals and bears his name.

We must immediately note that the equation of state for real gases which we are beginning to study is also approximate because to date there is no way of accurately calculating the forces of interaction between molecules.

**Account of Forces of Repulsion Between Molecules.** In the equation of state for ideal gases

$$pV = RT \tag{5.1}$$

written for one mole, by $V$ is meant the volume of the vessel containing the gas. At the same time, this is the volume available for each of the molecules of the gas travelling in this volume. When we are dealing with an ideal gas consisting of point molecules, there is no difference between the concepts "volume of the vessel" and "volume available for each molecule" because the point molecules do not hinder the movements of one another. Actually, however, not all of the volume of a vessel is at the disposal of the molecules because each of them occupies a definite part of the volume of the vessel, and this part is inaccessible for all the others.

To take this circumstance into account, we must subtract from the volume of the vessel the part of it that is not available for the motion of the molecules. Let us denote it by $b$. Equation (5.1) thus acquires the form

$$p(V - b) = RT \tag{5.2}$$

The introduced correction $b$ is the limiting volume which a gas would occupy at an infinitely great pressure. Indeed, rewriting Eq. (5.2) in the form

$$V - b = \frac{RT}{p} \tag{5.3}$$

we find that when $p = \infty$ we have $V - b = 0$, and the volume $V$ equals $b$.

**Calculation of the Constant *b*.** By introducing the constant $b$ into the equation of state, we took into consideration the circumstance that the molecules of a gas cannot approach one another to a distance equal to zero (even at an infinitely great pressure). Actually here account is taken of the existence of forces of repulsion between molecules which are exactly what prevents the molecules from approaching one another to a distance smaller than a certain minimum one. The latter distance determines what is called the size of a molecule. Hence, account of the size of the molecules actually means account at the same time of the forces of repulsion between the molecules of a gas, and the constant $b$ introduced into the equation of state may be considered as a characteristic of these forces.

If we adopt certain assumptions on the structure of molecules and on the nature of the forces acting between them, we can calculate the value of the constant $b$, i.e. the magnitude of that part of the volume of a vessel that is not available for any molecule because it is occupied by all the other molecules. The simplest way to do this is to assume that molecules are rigid spheres.

Imagine a vessel having the shape of a cube whose volume $V$ equals the volume occupied by one mole of a gas at the given pressure and temperature (Fig. 84). An edge of the cube therefore equals $\sqrt[3]{V}$. Let the diameter of a molecule be $d$, and its radius $r = d/2$.

Assume that initially our vessel contains only one molecule. The entire volume of the vessel is available for its motion (more exactly—for the motion of its centre) minus a layer with a thickness of $r$ adjoining the walls because the centre of the molecule cannot approach the walls by a distance less than $r$ (in Fig. 84 this layer is separated by a dash line). This means that our molecule can travel in a cube whose edge is less by $d$ than that of the actual cube—the vessel containing the gas. This volume is

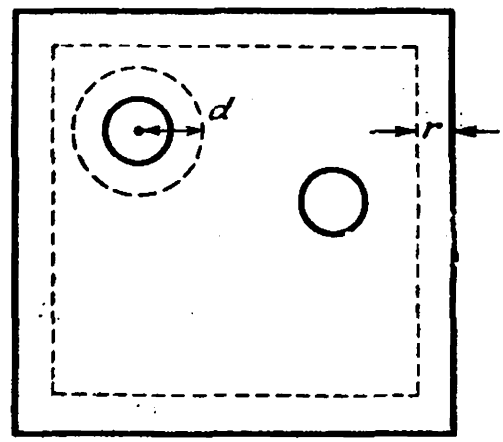


Fig. 84

$$(\sqrt[3]{V} - d)^3$$

Let us now introduce a second molecule into the vessel (this moment is shown in Fig. 84). The centre of either of the two molecules that are now in the vessel has at its disposal for motion the same volume as before, but minus the additional volume that has become inaccessible owing to the presence of the second molecule. In Fig. 84, the dash circle shows the volume surrounding each molecule into whose limits the centre of its partner cannot move. This volume equals $(4/3)\pi d^3$. Therefore, a volume equal to

$$(\sqrt[3]{V} - d)^3 - \frac{4}{3}\pi d^3$$

becomes accessible for either of the two molecules.

If we introduce a third molecule into our vessel, then the volume

$$(\sqrt[3]{V} - d)^3 - 2 \times \frac{4}{3}\pi d^3$$

will now be free for the motion of any of the three molecules in the vessel.

Finally, when all the $N_A$ molecules are in the vessel ($N_A$ is the Avogadro constant) that form one mole, each of them will be able to travel within the volume

$$(\sqrt[3]{V} - d)^3 - N_A \frac{4}{3}\pi d^3 \tag{5.4}$$

In these calculations, however, we omitted the circumstance that not one, but two molecules participate in each act of approachment (collision).

For each of them, not the entire forbidden sphere surrounding the second participant of the collision is of significance, but only that half of the sphere (the hemisphere) facing it. If we apply this reasoning to any pair of all the $N_A$ molecules, we must write $N_A/2$ instead of $N_A$ in expression (5.4). Consequently, the volume

$$V' = (\sqrt[3]{V} - d)^3 - \frac{N_A}{2}\frac{4}{3}\pi d^3$$

will be free for the motion of any molecule.

Since the diameter $d$ of a molecule is much smaller than an edge $\sqrt[3]{V}$ of our cubical vessel, i.e. $d \ll \sqrt[3]{V}$, then disregarding $d$, we get

$$V' = V - N_A\frac{2}{3}\pi d^3 = V - N_A\frac{16}{3}\pi r^3$$

This is exactly the quantity $V - b$ which we introduced instead of $V$ in equation of state (5.2). Hence,

$$b = \frac{16}{3}\pi r^3 N_A \qquad (5.5)$$

Therefore, the correction for the volume of the molecules equals not the volume of the molecules themselves, but the quadrupled value of this quantity.

We obtained this result considering the molecules to be rigid spheres. It must be noted that such a notion is a rough approximation. This can be seen from the fact that when the pressure tends to infinity, the volume of the gas should tend to the value $b$, as we have seen above. But in this case, the molecules should obviously be "packed" as dense as possible. With such packing, the spherical molecules actually occupy a greater volume than the sum of the volumes of all the spheres at the expense of the spaces between them. But it follows from geometrical considerations that the ratio of the volume occupied by all the spheres to their "pure" volume is $6/\pi\sqrt{2}$, i.e. less than two, whereas our calculations show that this ratio equals four. Nevertheless, when the pressure is not too great, our calculations give approximately correct results.

**Account of Forces of Attraction Between Molecules.** Apart from the forces of repulsion which have already been taken into account by introducing the correction $b$, forces of attraction also exist between molecules. These forces result in the fact that the pressure of the molecules of a gas on any area, for example on the walls of a vessel, will be less than in the case of an ideal gas, other conditions being equal.

Indeed, any molecule near the wall of a vessel where it has more "neighbours" at one side than at the other is subjected to the action of a result-

ant force exercised by the other molecules, and this force is directed into the gas. Owing to this, the pressure on the wall of the vessel will become smaller by a certain amount $\Delta p$ so that instead of Eq. (5.3) written in the form $p = RT/(V - b)$ we get the following equation for the pressure:

$$p = \frac{RT}{V-b} - \Delta p \quad \text{or} \quad p + \Delta p = \frac{RT}{V-b}$$

The forces of attraction between the molecules tend to bring them closer together. But the external pressure $p$ has exactly the same effect.

It is not difficult to establish what this additional pressure (or, which is the same, the reduction in the pressure on the wall) should depend on.

The pressure acting on the layer adjacent to the walls from the side of the molecules of the gas equals the force acting on all the molecules on a unit surface area of the layer. This force is obviously proportional to the density $n$ of the molecules. On the other hand, the number of molecules in the layer adjoining the walls subjected to the action of the force of attraction is also proportional to $n$. Hence, $\Delta p$ is proportional to $n^2$. Since $n$ is inversely proportional to the volume occupied by a mole of a gas, then $\Delta p = a/V^2$, where $V$ is the molar volume of the gas, and $a$ is a proportionality factor whose numerical value depends on the nature of the forces of attraction between the molecules. At present there are no ways of calculating this factor theoretically, and its values are found experimentally (see Sec. 5.9).

Thus, the expression for the pressure of a gas with account of the forces of attraction between the molecules can now be written in the form

$$p + \frac{a}{V^2} = \frac{RT}{V-b}$$

whence

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{5.6}$$

This equation relating the pressure, volume, and temperature of a gas is an equation of state for a real gas. It takes into account both forces of attraction (the correction term $a/V^2$) and forces of repulsion (the correction $b$) between the molecules. It is called the *van der Waals equation*. We shall see that this equation explains quite well the main experimental facts relating to real gases set out in the preceding sections.

Equation (5.6) relates to one mole of a gas. For an arbitrary amount of a gas, it acquires the form

$$\left(p + \frac{M^2}{\mu^2}\frac{a}{V^2}\right)\left(V - \frac{M}{\mu}b\right) = \frac{M}{\mu}RT \tag{5.7}$$

where $M$ = mass of the gas
$\mu$ = molecular mass of the gas
$V$ = volume occupied by the gas.

The factor $a$ in the expression for the pressure correction and the correction $b$ are considered to be constant quantities whose numerical values differ for different gases. Consequently, Eq. (5.6) is not a universal one to the same extent as the Clapeyron equation.

The constant $b$ is measured in units of volume. The dimension of the quantity $a$ is determined by the circumstance that the quantity $a/V^2$ must have the dimension of pressure. Hence, $a$ is measured in the units $\mathrm{N \cdot m^{-2} \cdot m^6 = N \cdot m^4}$ in the SI system, and in $\mathrm{dyn \cdot cm^4}$ in the cgs system. Sometimes $a$ is also measured in $\mathrm{atm \cdot cm^6}$.

## 5.7. VAN DER WAALS ISOTHERMS

The van der Waals equation after simple transformations can be given the form

$$pV^3 - (bp + RT)V^2 + aV - ab = 0$$

Dividing both sides of this equation by $p$, we get

$$V^3 - \left(b + \frac{RT}{p}\right) V^2 + \frac{a}{p} V - \frac{ab}{p} = 0 \qquad (5.8)$$

This is a cubic equation relative to the volume $V$, and it therefore has three roots. This means that at the given values of the temperature and pressure we can have three values of the molar volume or, which is the same, three values of the density of a gas.

The three roots of the cubic equation may be either all real, or two imaginary and one real. In a particular case with the corresponding values of the coefficients of the equation, all three real roots may equal one another (multiple roots); in this case, the left-hand side of the equation is an exact cube.

The imaginary roots of the van der Waals equation can have no physical meaning, and we shall give them no more attention.

To find the meaning of the roots of the van der Waals equation, we may simply consider the isotherms of Eq. (5.6), i.e. the dependence of the pressure $p$ on the molar (or specific) volume $V$ at a constant temperature, and compare them with the isotherms obtained experimentally.

Unlike the isotherm of an ideal gas, which is a hyperbola, the isotherm corresponding to Eq. (5.6), which we shall call the *van der Waals isotherm*, has the shape shown in Fig. 85. This curve, graphically depicting a cubic equation, has a maximum and a minimum so that three values of the molar volume — $V_1$, $V_2$, and $V_3$ — correspond to a given value of the pressure, for instance $p_1$. It is natural to consider that the *liquid state* corresponds to the minimum of these three values of the volume (the maximum density), and the *gaseous state* to the maximum value. It remains for us to determine the meaning of the third state with the volume $V_2$.

There is an appreciable difference between a van der Waals and an experimental isotherms, as can be seen from Fig. 86, where the solid line shows to an arbitrary scale the characteristic shape of an experimental isotherm, and the dotted line that of a van der Waals isotherm. A glance at the figure shows that instead of straight horizontal section *abc* of the experimental

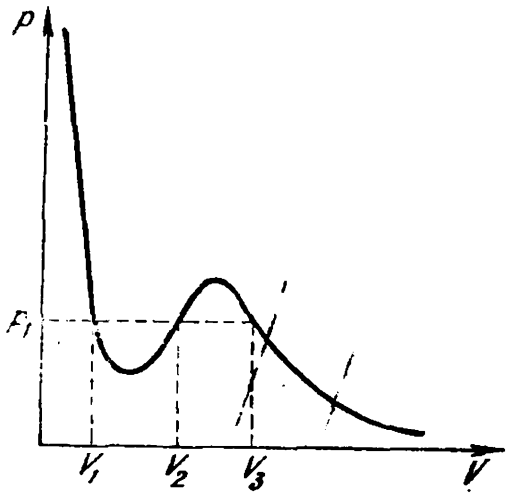



Fig. 85

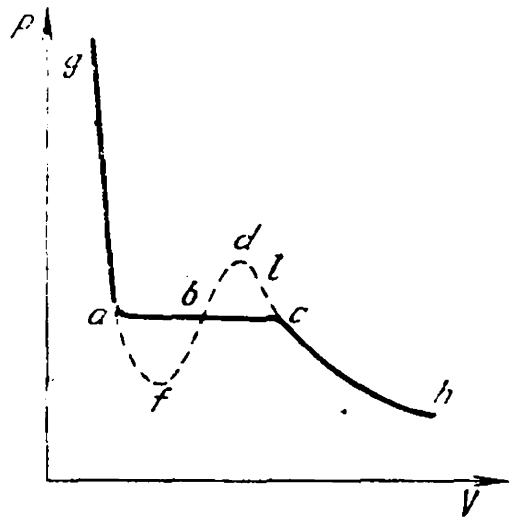



Fig. 86

isotherm, the van der Waals isotherm has a characteristic curl with a maximum and a minimum in this region.

This important difference is easily explained, however, upon proper analysis of the isotherm.

First of all we must note that sections *hc* and *ag* of the van der Waals isotherm coincide (at least qualitatively) with the corresponding sections of the experimental isotherm. We must remember here that section *hc* corresponds to the gaseous state, and section *ag* to a liquid. Consequently, the existence of two phases of a substance directly follows from the van der Waals equation. Then why don't we observe a third phase in experiments, depicted, for instance, by point *b* on the van der Waals isotherm?

It is easy to see that states corresponding to points on section *fbd* of the curve cannot exist because an unusual dependence of the volume on the pressure corresponds to this section: the volume grows instead of diminishing with increasing pressure. It is quite obvious that there are not and cannot be such substances in nature which would increase their volume upon a growth in the pressure, i.e. would reduce their density. The state of a substance with such strange properties should inevitably be extremely unstable.

Indeed, imagine that such a state has been realized in some way or other, and suppose that in a part of such a substance the pressure by chance has increased by an infinitely small amount. Such chance slight changes are not only possible, but are inevitable. This increase in the pressure should therefore lead to an increase in the volume which, in turn, will lead to a still greater growth in pressure, etc., until the substance passes over to the state

corresponding to point *d*, beginning from which the pressure dependence of the volume becomes qualitatively normal.

For the same reasons, an infinitely small chance diminishing of the pressure causes a spontaneous transition of the substance to the state corresponding to point *f*.

Thus, there is nothing surprising in that the states corresponding to section *fbd* which are possible according to the van der Waals equation are not actually observed. As regards the states corresponding to sections *cd* and *af* of the isotherm, then, although they are not unstable to such an extent, they are, however, less stable than the states corresponding to section *abc*. These states can even be achieved, but only in special conditions.

A substance whose states correspond to points on section *cd* of the curve (see Fig. 86) is in the gaseous state because section *cd* is a continuation of isotherm branch *hc*. But the pressure of the gas (vapour) in any of these states is higher than the saturated vapour pressure at the same temperature, which is unnatural.

This peculiar state of a substance is actually observed, for example, when a closed vessel with air containing water vapour is rapidly cooled. It is only necessary to thoroughly remove all traces of dust from the air and see that it contains no electric charges. In these conditions, notwithstanding the cooling and, consequently, the reduction in the pressure of the saturated water vapour, the latter during a quite long time does not condense, remaining in the gaseous state. It is exactly this state that corresponds to points on section *cd* when the vapour is in the *supersaturated* state, i.e. when its amount is greater than is needed for it to be saturated. Such a vapour is therefore called *supersaturated* or *supercooled*. In the long run after a certain time has elapsed, droplets of water will nevertheless appear on the walls of the vessel, indicating that the supersaturated vapour has decomposed into water and saturated vapour at the given, lower temperature. We shall explain on a later page why the state of a supersaturated vapour is less stable than that of a saturated vapour mixed with a liquid.

As regards the states of a substance characterized by points on section *af* of the van der Waals isotherm, these states are practically even more difficult to realize, again owing to their low stability.

Points on this section correspond to the liquid state — section *af* is a continuation of branch *ag*. This state of a substance is often called a *superheated liquid*. This name cannot be considered successful because it is generally applied to a liquid in an open vessel heated to above the boiling point but that does not boil. But such a liquid freely evaporates, i.e. its mass changes. What we are interested in here is the behaviour of a *definite mass* (for example one mole) of a liquid or vapour in a closed vessel when we cannot speak of boiling.

States corresponding to section *cd* and *af*, unlike the *unstable* states on section *fbd*, are called *metastable*.

Thus, we can explain the difference between the van der Waals and an experimental isotherms: the states corresponding to the root $V_2$ of the equation of state are not observed experimentally owing to their unstability or metastability. At a given temperature (for a given isotherm) only at one definite value of the pressure, namely, at the saturated vapour pressure, does a stable state — the state of a vapour in equilibrium with the liquid, i.e. a two-phase state — correspond to this root.

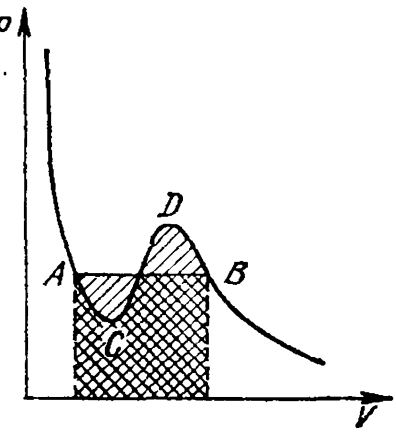


Fig. 87

We cannot determine the position of the horizontal section of the experimental curve relative to the maximum and minimum of the van der Waals curve using the van der Waals equation of state. This means that we cannot determine the value of the equilibrium pressure of the saturated vapour at a given temperature. We can do this, however, on the basis of general thermodynamic considerations. J. Maxwell showed that if we consider the transition from state $A$ to state $B$ (Fig. 87), then regardless of whether it occurs along the single-phase curve $ACDB$ or the two-phase straight line $AB$, it must be attended by the same work. Since the work in a graph in $p$-$V$ coordinates equals the area under the corresponding sections of the graph, the area under curve $ACDB$ should equal that under straight line $AB$. Hence it is obvious that straight line $AB$ is arranged so that the areas of the singly hatched regions (see Fig. 87) equal each other.

The importance of the van der Waals equation is not limited to its describing the fact of the existence of two phases of a substance — liquid and gaseous—in which the substance may be. We shall see in the following section that such an important fact as the existence of a critical temperature and a critical state directly follows from the van der Waals equation.

## 5.8. CRITICAL TEMPERATURE AND CRITICAL STATE

In the preceding section, we considered the van der Waals isotherm at a certain arbitrary temperature. Let us now see how these isotherms change with a change in temperature.

The general nature of the change in the van der Waals isotherms with temperature can be seen in Fig. 88 (the specific volume is laid off along the axis of abscissas). This figure shows as an example a number of isotherms for carbon dioxide. They were calculated using the following experimentally found values of the constants $a$ and $b$:

$$a = 3.6 \times 10^{-6}\ \text{atm} \cdot \text{m}^6/\text{mol} \quad \text{and} \quad b = 42.8 \times 10^{-6}\ \text{m}^3/\text{mol}$$

How these constants are determined experimentally will be discussed in Sec. 5.9.

Inspection of the curves in Fig. 88 shows that the isotherms are arranged higher in the graph with increasing temperature, which is quite natural, and, in addition, the maxima and minima of the isotherms become closer

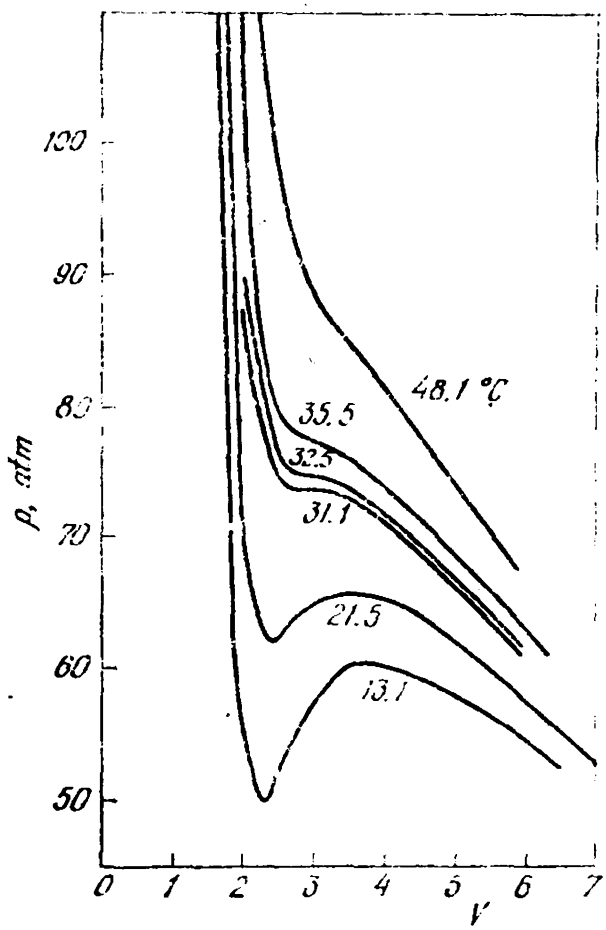



Fig. 88

to each other both along the axis of abscissas (the difference between the volumes corresponding to them diminishes) and along the axis of ordinates (the corresponding difference between the pressures diminishes). Finally, at a quite definite temperature (31.1 °C in Fig. 88), the maximum and minimum of the isotherm merge and degenerate into a point of inflection at the values of $V = 0.94 \times 10^{-4}$ m³/mol and $p = 73$ atm. This means that elevation of the temperature is attended by a gradual diminishing of the difference between the three values of the volume corresponding to the same value of the pressure, i.e. the difference between the three roots of the van der Waals equation diminishes.

At a definite temperature $T_{cr}$, all three values of the volume merge (the roots of the equation become multiple). At this temperature, consequently, the difference between the various states of a substance vanishes. This is obviously the critical temperature whose existence, as we have seen, is a characteristic property of a substance.

It is not difficult to calculate the value of the critical temperature $T_{cr}$ and the values of the two other critical parameters — the critical volume $V_{cr}$ and the critical pressure $p_{cr}$ — corresponding to it.

Indeed, the left-hand side of the van der Waals equation (5.8) at the values of $T = T_{cr}$ and $p = p_{cr}$, i.e. the expression

$$V^3 - \left(b + \frac{RT_{cr}}{p_{cr}}\right) V^2 + \frac{a}{p_{cr}} V - \frac{ab}{p_{cr}}$$

should be an exact cube, and can therefore be written in the form:

$$V^3 - \left(b + \frac{RT_{cr}}{p_{cr}}\right) V^2 + \frac{a}{p_{cr}} V - \frac{ab}{p_{cr}} =$$

$$= V^3 - 3V_{cr}V^2 + 3V_{cr}^2 V - V_{cr}^3 \qquad (5.9)$$

This equation is identically observed if the coefficients of identical powers of $V$ in both of its sides are equal to each other:

$$b + \frac{RT_{cr}}{p_{cr}} = 3V_{cr}, \quad \frac{a}{p_{cr}} = 3V_{cr}^2, \quad \text{and} \quad \frac{ab}{p_{cr}} = V_{cr}^3$$

By solving this system of equations, we get the values of the critical parameters expressed through the constants $a$ and $b$:

$$p_{cr} = \frac{a}{27b^2}, \quad V_{cr} = 3b, \quad \text{and} \quad T_{cr} = \frac{8a}{27Rb} \qquad (5.10)$$

The same results and some other conclusions can be obtained from a more detailed mathematical analysis of the van der Waals equation. For this purpose, let us write it in the form

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \qquad (5.11)$$

Let us first find the values of the volume corresponding to the maximum and minimum on the van der Waals isotherm. At both these points, the first derivative of the pressure with respect to the volume equals zero, i.e. $\partial p/\partial V = 0$.

Differentiating Eq. (5.11) and equating the derivative to zero, we get

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = \frac{2a}{(V-b)^2}\left[\frac{(V-b)^2}{V^3} - \frac{RT}{2a}\right] = 0 \qquad (5.12)$$

Hence, the condition that $\partial p/\partial V = 0$ is observed when

$$\frac{(V-b)^2}{V^3} = \frac{RT}{2a} \qquad (5.13)$$

This equation is cubic. It therefore follows that for any $T$, i.e. for any isotherm, there are three values of $V$ at which it passes through a maximum or a minimum. One of these values evidently corresponds to the minimum,

and the other to the maximum on the isotherm. We convinced ourselves that they exist when we had directly plotted the isotherms. As regards the third value, i.e. the third extremum, it is in the region $V < b$ and is therefore deprived of a physical meaning.

We shall now show that at a certain value of the temperature $T = T_{cr}$ the maximum and minimum of the isotherm merge and that the curve has a point of inflection at the point of their merging, i.e. that the second derivative also equals zero at this point.

For this purpose, we shall find the value of the second derivative $\partial^2 p/\partial V^2$ at the points where the first derivative equals zero. The second derivative of $p$ with respect to $V$ is

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \tag{5.14}$$

Condition (5.13) is observed at the points where $\partial p/\partial V = 0$. Substituting for $T$ in Eq. (5.14) its value found from Eq. (5.13), we get

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_{\frac{RT}{2a}=\frac{(V-b)^2}{V^3}} = \frac{2a(3b-V)}{V^4(V-b)} \tag{5.15}$$

Hence it follows that $\partial^2 p/\partial V^2 = 0$ when $V = 3b = V_{cr}$.

If we introduce this value of $V$ in Eq. (5.13), then for $T$ at the point of inflection we get $T = 8a/27Rb = T_{cr}$.

Thus, at $T = T_{cr} = 8a/27Rb$ and $V = V_{cr} = 3b$, the van der Waals isotherm has a point of inflection at which $\partial p/\partial V = 0$ and $\partial^2 p/\partial V^2 = 0$.

Hence, $T_{cr} = 8a/27Rb$ is obviously the critical temperature.

It follows from Eq. (5.12) that when $T > T_{cr}$ the derivative $\partial p/\partial V$ is less than zero in all conditions because when $T = T_{cr}$ the expression in brackets in Eq. (5.12) equals zero. This means that above the critical temperature $T_{cr}$ the isotherm is a monotonously falling curve (the derivative is always negative).

The value of the critical pressure $p_{cr}$ is obtained from the van der Waals equation itself if we use the found values of $T_{cr}$ and $V_{cr}$ in it:

$$p_{cr} = \frac{a}{27b^2}$$

We have thus obtained Eqs. (5.10) for the critical parameters in a different way.

In a similar way, we can find the change in the distance between the maximum and the minimum when passing from one isotherm to another. For this purpose, it is sufficient to get an equation of the curve passing through

the maxima and minima of the isotherms. It is shown by a dash line in Fig. 89 (we have seen above that this curve separates the region of two-phase states).

It is clear that points on this curve must simultaneously obey the van der Waals equation (5.11), i.e. $p=\frac{RT}{V-b}-\frac{a}{V^2}$, and Eq. (5.13). Deleting $T$ from these two equations, we get the expression we are interested in:

$$p = \frac{a(V-2b)}{V^3} \qquad (5.16)$$

This is exactly the equation of the curve passing through the maxima and minima of the isotherms. We shall find the maximum of this curve if we take the derivative with respect to $V$ and equate it to zero:

$$\frac{\partial p}{\partial V} = \frac{2a(3b-V)}{V^4} = 0 \qquad (5.17)$$

Hence,

$$V = 3b = V_{cr}$$

i.e. the maximum of the dash curve coincides with the point of inflection of the critical isotherm which, as we have learned, corresponds to the value $V_{cr} = 3b$.

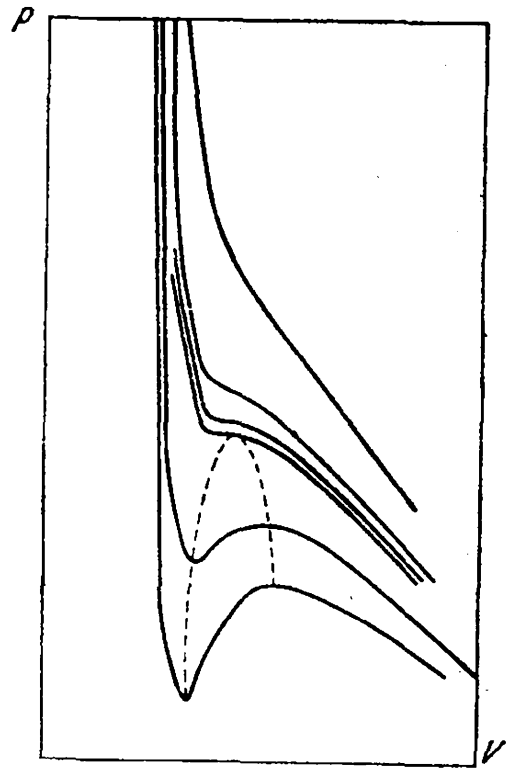


Fig. 89

Let us note in conclusion that the compressibility of a substance at the critical point equals infinity. Indeed, by Eq. (2.37) the compressibility is

$$\varkappa = \frac{1}{V}\frac{\partial V}{\partial p}$$

But since at the critical point we have $\partial p/\partial V = 0$, then $\partial V/\partial p = \infty$, and therefore $\varkappa = \infty$.

## 5.9. EXPERIMENTAL DETERMINATION OF THE VAN DER WAALS EQUATION CONSTANTS

The values of the constants $a$ and $b$ can be calculated with the aid of Eqs. (5.10) relating these constants to the critical parameters. The latter, in turn, are determined experimentally as described in Sec. 5.5. This method is not distinguished for its accuracy, particularly because it is exactly near the critical temperature that the van der Waals equation is not obeyed with sufficient accuracy.

A more accurate way of determining the constants $a$ and $b$ consists in measuring the temperature dependence of the pressure of a gas at constant

volume. For this purpose, it is only necessary to place the gas being studied into a closed vessel having the volume $V_0$ and provided with a manometer, and measure the pressure of the gas at different temperatures. After getting a curve $p = f(T)$ from these experiments, we find the quantity $(\partial p/\partial T)_V$. (The subscript $V$ relating to the partial derivative indicates that the volume of the gas is kept constant.) It follows from the van der Waals equation that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}$$

($R$ is the molar gas constant). Hence,

$$b = V - \frac{R}{\left(\frac{\partial p}{\partial T}\right)_V} \tag{5.18}$$

The constant $a$ is determined from the van der Waals equation after introducing into it the value of $b$ obtained from Eq. (5.18):

$$a = V^2\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \tag{5.19}$$

It must be remembered that in the above equations the quantity $V$ stands for the molar volume:

$$V = \frac{V_0\mu}{M}$$

where $V_0$ = volume of the vessel
$M$ = mass of the gas in the vessel, which should be determined by weighing
$\mu$ = its molecular mass.

The above experiment should be conducted at a sufficiently high pressure of the gas so as to already observe an appreciable deviation from Gay-Lussac's law according to which

$$\frac{\partial p}{\partial T} = \frac{R}{V}$$

In other words, the experiment should be conducted at such pressures when the value of $b$ is already an appreciable fraction of $V$.

## 5.10. COMPARISON OF VAN DER WAALS EQUATION WITH EXPERIMENTAL DATA

Although the van der Waals equation correctly describes the main phenomena connected with the change in the density of a gas accompanying a change in its pressure and temperature, as well as the mutual transitions

of a liquid and a gas, there are also important deviations from this equation. This relates first of all to a quantitative comparison of theory and experimental data.

We find, first, that what we called the constants $a$ and $b$ in the van der Waals equation are not at all constants. The experiments described in the preceding section show that $a$ and $b$ depend on the temperature. This can be seen, for example, from Table 14 compiled for argon. According to the meaning of the van der Waals equation, however, the quantities $a$ and $b$ should be constants with characteristic values for a given substance.

*Table 14*

**Temperature Dependence of Constants $a$ and $b$ for Argon**

| Temperature, K | $a$, kg·m⁵/s² | $b \times 10^6$, m³/mol | Temperature, K | $a$, kg·m⁶/s² | $b \times 10^6$, m³/mol |
|---|---|---|---|---|---|
| 424 | 0.192 | 61.0 | 466 | 0.169 | 51.0 |
| 430 | 0.187 | 59.5 | 486 | 0.160 | 48.0 |
| 436 | 0.184 | 58.0 | 506 | 0.153 | 45.0 |
| 446 | 0.179 | 55.5 | 526 | 0.147 | 43.0 |
| 456 | 0.174 | 53.0 | 546 | 0.142 | 41.0 |

The difference between isotherms obtained experimentally and those calculated according to the van der Waals equation is also connected with this circumstance. We can naturally so choose the values of the constants $a$ and $b$ that the theoretical and experimental isotherms will coincide at one definite value of the temperature. But in this case the isotherms for all other values of the temperature will not coincide.

Another quantitative deviation between the theoretical equation and the experimental data is connected with the values of the critical parameters $p_{cr}$, $V_{cr}$, and $T_{cr}$. It follows from Eqs. (5.10) that there should be a universal relationship between these quantities which does not depend on the nature of a substance:

$$\frac{RT_{cr}}{p_{cr}V_{cr}} = \frac{8}{3} = 2.67$$

Experiments show, however, that although the quantity $RT_{cr}/p_{cr}V_{cr}$ is more or less constant for many substances, it equals not 2.67, but approximately 3.7.

Finally, experiments show that the equation $V_{cr} = 2b$ is obeyed much better than $V_{cr} = 3b$ following from the van der Waals equation.

We shall not stop here to consider other shortcomings of the van der Waals equation. It is quite clear from the above examples that this equation is only approximately true and is suitable only for rough quantitative

assessments of the relationships between the parameters determining the state of a real substance.

We shall also omit here the numerous more accurate equations of state. Their better coincidence with experimental data is the result of the introduction of a greater number of constants in them (the van der Waals equation has two such constants). The physical meaning of the constants, however, is not so clear as in the van der Waals equation.

At present, it is customary practice to describe the state of a real gas by a more general equation in the form of the series

$$pV = RT + \frac{B}{V} + \frac{C}{V^2} + \cdots \tag{5.20}$$

(in essence it is the expansion of the expression for the pressure by the powers of $1/V$, i.e. the density). The coefficients $B$, $C$, . . . , which have to be determined experimentally, are called the *virial coefficients*. Generally speaking, they depend on the temperature.

If in Eq. (5.20) we limit ourselves to the first two terms, then when $B = b - (a/RT)$ and provided that $b/V \ll 1$, Eq. (5.20) transforms into the van der Waals equation.

## 5.11. REDUCED VAN DER WAALS EQUATION. LAW OF CORRESPONDING STATES

Isotherms plotted for the same temperature for different gases naturally have a different appearance because the constants $a$ and $b$ and the critical quantities $p_{cr}$, $V_{cr}$, and $T_{cr}$ related to them differ for different gases. Remember that the isotherms of ideal gases do not depend on the individual properties of the gases (if the isotherms are plotted for one mole).

We can also write the equation of an isotherm for real gases, however, so that it will not depend on the nature of a gas, i.e. will be universal. For this purpose, the parameters of state must be in identical ratios to the relevant critical parameters. In other words, any gases with identical (or, as is said, corresponding) ratios

$$\frac{p}{p_{cr}} = \pi, \quad \frac{V}{V_{cr}} = \omega, \quad \text{and} \quad \frac{T}{T_{cr}} = \tau \tag{5.21}$$

will be described by identical equations. The dimensionless parameters $\pi$, $\omega$, and $\tau$ are called *reduced parameters*.

Let us substitute for $p$, $V$, and $T$ in the van der Waals equation (5.6), i.e.

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

their values $\pi p_{cr}$, $\omega V_{cr}$, and $\tau T_{cr}$ found from Eqs. (5.21), and then introduce instead of the critical parameters $p_{cr}$, $V_{cr}$, and $T_{cr}$ their values given in Eqs. (5.10). We get

$$\left(\pi + \frac{3}{\omega^2}\right)\left(\omega - \frac{1}{3}\right) = \frac{8}{3}\tau \qquad (5.22)$$

This equation contains no constants characterizing an individual substance. It is therefore a universal equation holding for all substances.

Equation (5.22) is called the *reduced equation of state*. It follows from this equation that if substances have *two* identical reduced parameters of three, then the *third* parameter is also identical for these substances. This law is called the *law of corresponding states*. It expresses the fact that by changing the scale used to measure two of the three parameters (for example $p$ and $V$) characterizing the state of a substance, i.e. by using the reduced parameters, we can make the isotherms of all substances coincide.

The law of corresponding states is also approximate, although its accuracy is somewhat higher than that of the van der Waals equation itself because it does not depend on the concrete form of the equation of state.

The law of corresponding states can be used to calculate unknown isotherms for various gases if their critical parameters are known and the isotherms of other gases have been measured.

## 5.12. INTERMOLECULAR FORCES OF INTERACTION IN A REAL GAS

When we studied the properties of an ideal gas, its particles were considered to have no interaction. But upon the collisions that also occur in an ideal gas such interaction actually does exist. It has a quite definite nature in an ideal gas: forces of repulsion act between the molecules at very small distances, and the diameter of the particles is determined by these forces. When the centres of the molecules are separated from one another by distances more or less appreciably exceeding the diameter, these forces do not virtually manifest themselves any longer, and the molecules move freely (rectilinearly and uniformly) over their free path, i.e. up to the next collision.

Our notion of molecules as of rigid spheres which we have repeatedly used means that at distances between their centres equal to their diameter the force of repulsion equals infinity so that further approach is impossible, whereas when the distance between molecules exceeds their diameter, no forces whatsoever act between the molecules of an ideal gas. Hence, in an ideal gas, the interaction between its molecules consists only in the action of forces of repulsion at small distances.

In a real gas, these forces of repulsion with small distances between the molecules also act, of course, but in addition to them forces of attraction act between the molecules of a real gas, and we have taken them into account

by introducing a correction to the pressure in the equation of state. We can say about a real gas that its molecules interact at any distances at which they may be in such a gas. It is exactly this circumstance which distinguishes a real gas from an ideal one.

The forces of interaction between molecules are in their nature electrical ones due to the atoms and, consequently, the molecules containing electrically charged particles — electrons and nuclei. Since charges of like signs repel each other and those of opposite signs attract each other, it is very simple to explain the existence of forces of attraction and repulsion between the molecules.

It was found, however, that the forces of interaction between molecules cannot be described and calculated only on the basis of the laws of the electrostatic interaction of charges. The change from the repulsion of molecules at small distances to their attraction when the distance increases can only conditionally be explained as a result of the simultaneous existence of two kinds of forces. Calculation of the forces of interaction between molecules and first of all of the dependence of these forces on the distance between the molecules is possible only with the aid of quantum mechanics.

These forces vary considerably for different substances. This is exactly the reason why the constants $a$ and $b$ of the van der Waals equation differ so considerably, as do the critical parameters, especially the critical temperatures, related to them. For example, substances between whose molecules the smallest forces of attraction act (hydrogen and helium) have the lowest critical temperatures.

Theory and experiments show that the forces of attraction and repulsion depend very greatly on the distances between the centres of molecules.It can be roughly considered that both forces are inversely proportional to a certain power of the distance $d$ between the molecules:

$$F \propto \frac{1}{d^m}$$

The difference between the forces of attraction and repulsion apart from their sign lies in the value of the exponent of $d$. For forces of attraction (van der Waals forces), $m \approx 7$ so that $F \propto 1/d^7$.

For forces of repulsion, $m$ takes on values from 9 to 15. Both forces consequently diminish exceedingly rapidly with an increasing distance between the molecules, but the forces of repulsion diminish especially rapidly. Therefore, they may play an appreciable part only upon direct proximity of the molecules. It is exactly for this reason that the model of a rigid sphere gives approximately correct results.

## 5.13. HEAT CAPACITY OF REAL GASES

We have seen (Secs. 2.5 and 2.6) that for *ideal* gases the molar (or specific) heat capacity depends neither on the temperature nor on the volume occu-

pied by the gas. This is connected with the fact that the internal energy $U$ of an ideal gas does not depend on the volume occupied by a mole (or unit mass) of the gas, i.e. on its density, and is determined only by the temperature. But this holds only for an ideal gas. For a real gas, as for any body in general, the internal energy $U$ may depend not only on the temperature, but also on the volume occupied by a given mass of the gas (see Sec. 6.13). The explanation is that in real gases the internal energy is the sum of the *kinetic* energy of the molecules depending on the temperature and the *potential* energy that naturally depends on the mutual distance between molecules, i.e. on the density.

Consequently, for real gases, the internal energy $U$ of one mole is a function of the temperature $T$ and the volume $V$ it occupies:

$$U = f(T, V)$$

In this case, the molar heat capacity $C = dQ/dT$ can no longer be expressed by the simple equations (2.11), (2.12), or (2.17), (2.18).

Let us try to calculate the heat capacity of a real gas. We shall substitute for $dQ$ in Eq. (2.6) its expression according to the first law of thermodynamics $dQ = dU + dW$. Hence,

$$C = \frac{dU + p\,dV}{dT}$$

But now the change in the internal energy $dU$ consists of two parts: (1) a part depending only on the change in the temperature at constant volume, which we shall denote by $(dU)_V$, and (2) a part $(dU)_T$ depending only on the change in the volume at constant temperature. It is evident that

$$(dU)_V = \left(\frac{\partial U}{\partial T}\right)_V dT$$

where $(\partial U/\partial T)_V$ is the change in the internal energy per unit temperature change at constant volume. Similarly,

$$(dU)_T = \left(\frac{\partial U}{\partial V}\right)_T dV$$

Hence,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Correspondingly, the heat capacity $C$ will be

$$C = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\frac{dV}{dT} \qquad (5.23)$$

Equation (5.23) for the heat capacity is a *general* one suitable for all isotropic bodies. It differs from the previously obtained expression for the heat capacity of ideal gases (2.11) in that it includes the addend $\left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT}$ which equals zero for an ideal gas because $(\partial U/\partial V)_T = 0$. For the heat capacity at constant volume $C_V$, we get from Eq. (5.23) a known expression:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (dV = 0) \tag{5.24}$$

The heat capacity at constant pressure is

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p =$$

$$= C_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{5.25}$$

All the quantities in the right-hand side of Eq. (5.25) can be measured experimentally except for $(\partial U/\partial V)_T$ which does not lend itself to experimental measurement.

It can be shown, however, as will be done in the following chapter, that the quantity $(\partial U/\partial V)_T$ characterizing the change in internal energy with a change in volume (density) is related by a simple expression to the change in pressure caused by heating a gas at constant volume which is easy to measure. It is found that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Using this expression in Eq. (5.25), we get

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \tag{5.26}$$

and, accordingly,

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

As should be expected, for an ideal gas,

$$T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = R$$

which directly follows from the equation $pV = RT$. For *real* gases, the difference in heat capacities $C_p - C_V$ may appreciably differ from $R$.

CHAPTER 6

# ELEMENTS OF THERMODYNAMICS

## 6.1. EQUILIBRIUM STATES

The kinetic theory of gases gives a good explanation of many phenomena in ideal gases in which the movements of the molecules owing to the small values of the forces of interaction between them may be considered to be free. When we find it impossible to ignore the forces of interaction as for example in real gases, the theory describes the phenomena occurring in them with considerably less accuracy. This is explained by the fact that in the majority of cases we do not have at our disposal a detailed picture of the molecular movements because we do not succeed in taking a sufficiently accurate account of all the forces acting on the molecules. Any molecular system consists of a huge number of continuously moving molecules that interact with one another and constantly change their mutual arrangement. In such conditions, we cannot know exactly the forces acting at any moment on the molecules and, therefore, their movements. This is the reason why we also cannot determine theoretically the relationship between molecular movements and the properties of a substance.

Nevertheless, a number of properties of a substance and many phenomena in it can be studied even without a detailed knowledge of the mechanism of molecular movements if we use only macroscopic quantities, i.e. quantities characterizing a substance as a whole but having no meaning when applied to separate particles. Such quantities include first of all the pressure and temperature. We have already seen that these quantities have a meaning only with respect to a complex of a very great number of particles. We cannot speak of the pressure or temperature of one molecule. This follows already from the fact that both these quantities are determined by the mean kinetic energy of the particles.

We encountered a similar state of affairs in mechanics. In solving a number of problems relating to purely mechanical motion, we also find it difficult to determine the main parameters characterizing this motion, i.e. the coordinates and momenta of separate bodies of a system at any

moment. Here the general laws relating to the system as a whole come to our aid. They include the laws of conservation of energy and momentum. They can be used without knowing the detailed nature of interaction of bodies and their motion because these laws hold for any motion and any interactions.

Similarly, when studying the properties of a substance connected with the thermal movements of particles, we also use general laws that are always true regardless of the nature of the movements of the molecules, the interaction between them, and the structure of the substance. These general laws relate to energy, its changes, and to quantities related to it.

The branch of physics that studies the general properties of a substance connected with thermal motion in conditions of equilibrium is called *thermodynamics.*

The special place occupied by thermodynamics in physics is due to the fact that for reasons which will be treated below any form of energy upon its transformations changes in the long run into the energy of thermal motion. If, for instance, in the process of mechanical motion the energy of a body or a system of bodies diminishes owing to the action of friction forces, this occurs because it transforms into heat — rubbing bodies become heated. The energy of an electric current, of light, of chemical reactions, etc. also transforms into heat. Any kind of energy in the course of its transformations may pass through many forms, but the final result of all such transformations is without fail heat energy.

The conversion of mechanical energy into heat and the reverse process of obtaining mechanical work at the expense of thermal energy are of the greatest practical interest. Let us consider this question in greater detail.

But before beginning to do so and to formulate the laws of thermodynamics, we must give some attention to the important matter of *equilibrium* — a concept that is introduced into thermodynamics in the same way as is done in mechanics.

By equilibrium in mechanics is meant such a state of a body in which it is at rest (naturally relative to a system of coordinates). In thermodynamics, the concept of equilibrium is somewhat broader.

*A system is in thermodynamic equilibrium if the macroscopic quantities determining its state remain constant* (and, we shall add, equal to their mean values). This relates first of all to the pressure and temperature. Consequently, such phenomena as thermal conductivity, diffusion, chemical reactions, and phase transitions cannot occur in the state of equilibrium.

But thermodynamic equilibrium (it is sometimes also called *statistical equilibrium*) appreciably differs from its mechanical counterpart in that although the macroscopic quantities characterizing a system remain constant, the particles which the system consists of (atoms, molecules) do not stop their complicated movements. The circumstance that this does not keep the system from remaining in an unchanged state is due to the great number of the particles.

For example if two bodies having identical temperatures are brought into contact, we know from our everyday experience that no heat will pass from one body to the other. The temperatures of the bodies in contact will remain unchanged, and the bodies will be in equilibrium. At the same time, the particles of one of the bodies may have a greater kinetic energy than those of the other one at separate points of contact between them. At these points, heat will naturally transfer from one body to the other. But it will be compensated without fail by a reverse transition at other points where the difference between the energies has the reverse sign.

In sum, thermal energy will not pass from one body to another when the bodies have the same temperature. This should be ascribed to the fact that the particles along the contact surface, while having the most diversified "individual" energies, have mean energy values that are the same for both bodies.

The same relates to the well-known fact that in the state of equilibrium a gas is distributed uniformly throughout the entire volume of a vessel so that its density at all parts of the vessel is the same. The only reason for this is that the gas contains an exceptionally great number of molecules. If, for example, a vessel contained only 100 molecules, then upon a completely chaotic nature of the molecular movements we could not expect that the two halves of the vessel contain exactly 50 molecules each at any moment. But even with a great number of particles, some deviations from their uniform distribution throughout the volume may occur in separate parts of the vessel. Only the mean density of the gas in the entire volume is the same and constant.

Matters are similar when equilibrium is established between a liquid and a vapour in a closed vessel. The vapour over the liquid is formed as a result of evaporation (vaporization) — a process consisting in that molecules of the liquid having a high velocity leave the liquid through its surface. But part of the molecules that have escaped from the liquid may return to it during their chaotic motion, and this occurs the more frequently, the greater is the amount of vapour that has formed. Equilibrium sets in between a liquid and its vapour when the number of molecules leaving the liquid in a unit time becomes equal to their number returning to it from the vapour. The vapour becomes saturated, and after this no macroscopic changes occur in the system — the pressure and temperature remain constant. Molecules continue to leave the liquid and return to it from the vapour, however, even after equilibrium sets in. Here also in the state of equilibrium, the density of the vapour in separate parts of the volume may differ somewhat from the mean value, i.e. from the density of the saturated vapour.

These examples point to two features of the equilibrium state. First, the concept of thermodynamic equilibrium is an idealization to a certain extent because, strictly speaking, the parameters of state in equilibrium do

not remain constant, but fluctuate somewhat about their equilibrium (mean) values (see Sec. 1.7). Second, we can speak of thermodynamic equilibrium only when a system is composed of a very great number of particles.

We must stress the fact that the laws of thermodynamics which will be discussed in the present chapter relate only to systems consisting of a great number of particles.

## 6.2. REVERSIBLE AND IRREVERSIBLE PROCESSES

If a system for some reason or other is not in a state of equilibrium or has been brought out of it and then left alone (this means that it is not subjected to the action of external forces), experiments show that a transition to an equilibrium state occurs spontaneously. We can even say that the state of equilibrium is such a state into which any molecular system passes in the absence of external forces acting on it. The process of transition to equilibrium is called *relaxation*, and the time needed for this transition is called the *relaxation time*.

But when equilibrium has already set in, a system, as proved by experiments, cannot by itself return to the initial non-equilibrium state. In other words, the changes in state that occurred in a system while passing into the state of equilibrium cannot take place in the reverse direction without any external action.

For example, if two contacting bodies originally had different temperatures and were left alone, in the long run the temperatures of both bodies level out. But the reverse process — an increase in the difference between their temperatures — does not occur without any external action.

A gas left alone will always become distributed uniformly throughout the entire volume of the vessel it occupies, and such a state corresponds to equilibrium. But a gas never accumulates in one part of a vessel in a greater amount (with a greater density) than in another without the action of external forces.

In exactly the same way, if two different gases are introduced into a vessel, then owing to mutual diffusion they will mix by themselves, and the composition of the mixture will become identical throughout the vessel. This will be an equilibrium state. But to again separate these gases, considerable external forces will have to be used.

The above examples point to an important feature of processes occurring in molecular systems — to their *irreversibility*. In this respect, molecular processes differ from purely mechanical ones for which strict *reversibility* is the rule.

*Such a change in the state of a system (or of one separate body) is called a reversible process which when conducted in the reverse direction returns the system to the initial state so that it passes through the same intermediate*

*states as it did in the forward process, but in the reverse sequence, while the state of bodies outside of the system remains unchanged.*

All the motions considered in mechanics are *reversible* except those in which forces of friction participate (the action of friction forces results in the liberation of heat, and the process stops being purely mechanical).

For instance, when a quite elastic ball drops onto a hard surface, the potential energy of the ball transforms into kinetic energy. By the moment when the ball touches the surface onto which it is dropping, its kinetic energy exactly equals the initial potential energy if there is no friction against the air when the ball is moving downward. Elastic forces appear upon the impact (owing to deformation of the ball and the surface) and if the process is not interrupted, these forces will make the ball begin reverse motion upward. Here again, potential energy, this time the energy of deformation, will transfer into the kinetic energy of the motion of the ball, and it will rise to the same height from which it began to drop. This process may repeat many times. It is quite clear that the upward motion of the ball is a process that is the reverse of dropping, and it is not difficult to note that the ball when rising passes through the same intermediate states determined by its coordinates and velocities as in falling, but in the reverse sequence. Consequently, this purely mechanical process is reversible.

True, the process will proceed in the way we have just described it only if forces of friction against the air are absent, if the ball is completely elastic, and if the surface which it falls onto is also completely elastic. All these "ifs" show that a reversible process even in the mechanical example considered above is a certain idealization because actually no completely elastic bodies exist, forces of friction cannot be completely eliminated, and so on. But mechanical motions, at least in principle, are reversible.

Processes that do not comply with the condition of reversibility indicated above are called *irreversible*.

We shall give an example here which will permit us to define more precisely the concept of the reversibility and irreversibility of changes or processes.

Let a spring having one end fixed be deformed (stretched) by the force $F$ applied to its other end (Fig. 90). The spring stretches, increasing its po-

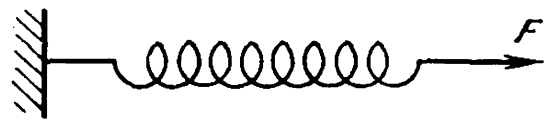



Fig. 90

tential energy at the expense of the work of the force $F$. If after the spring has been stretched over a definite length we stop the action of the force, then the spring will return to its initial state, correspondingly reducing its potential energy. May we consider that the above process of stretching the spring is reversible?

It is easy to see that if we stretch the spring rapidly (we will see below what is meant by "rapidly") and immediately stop the action of the force, then the process will not be reversible.

Indeed, when the force $F$ begins to stretch the spring, that part of the latter which the force is directly applied to, i.e. the part adjoining the free end, is deformed first of all. The deformation is gradually transmitted to the remaining parts of the spring, and its part adjoining the fixed end is deformed the last.

After the action of the force stops, the spring begins to contract. But now too the part of the spring adjoining the point of application of the force will be the first subjected to deformation, this time to deformation of compression, because it will obviously be the first to "feel" that the force stopped acting. From this part, the deformation will gradually be transmitted along the spring until the initial state is restored.

Thus, although the process of contraction does proceed in the reverse direction, the spring does not pass through the intermediate states in the reverse sequence: in the forward process first the part of the spring adjoining its free end deformed, and the deformation spread to the remaining parts of the spring from it; the spring deformed in contraction in the same, and not in the reverse, order. Therefore in the above experiment, we cannot consider that the spring stretching process is reversible. Irreversibility will tell in that upon rapid stopping of the action of the force oscillatory motion of the spring will begin which is not reversible: friction forces will result in attenuation of the oscillations, and their energy will transform into heat.

For the same reason, rapid compression or expansion of a gas — isothermal or adiabatic — is not a reversible process. As when considering the spring, irreversibility here consists in that the alternation of the intermediate states in the forward and reverse processes is the same.

Irreversible processes also include the expansion of a gas into a vacuum, which is not balanced by external forces. All the transport phenomena — thermal conductivity, diffusion, and internal friction — are irreversible.

## 6.3. QUASISTATIC PROCESSES

In connection with the concepts of reversibility and irreversibility, we would like to remind our readers what was said in Sec. 2.4 about quasistatic processes (p. 103).

Processes that proceed irreversibly in one set of conditions may sometimes be reversible in another one. For example, the spring stretching process described above may also be conducted reversibly. For this purpose, it is necessary that the external force stretching the spring should continuously grow during the stretching so that at each given moment it would be equal and opposite to the elastic force of the spring itself. In other words, it is essential that at each given moment the spring be in a state of equilibrium. For this purpose, the stretching should be conducted at such a slow rate

that there will be time for the deformation to be transferred along the entire length of the spring and to be the same all the time and at all points. Now the spring will be in equilibrium at any moment. In principle, the process must be conducted infinitely slowly. Actually, the duration of stretching should be greater than that of relaxation. If the duration of the process is less than the relaxation time, there is no time for equilibrium to set in, the process is too rapid to be reversible.

It should be remembered that *processes in which a system constantly remains in a state of equilibrium are called quasistatic.* It is quite clear that such processes are reversible because all the intermediate states are equilibrium ones.

In the above examples of the contraction (compression) and stretching (expansion) of a spring or a gas, the relaxation time is the time needed for the propagation of sound because sound waves are stretchings and contractions propagating in a body.

The expansion of a gas or its compression performed, for example, with the aid of a piston, will be quasistatic if the velocity of the piston is small in comparison with the velocity of sound in the gas because in this condition the pressure has time to level out throughout the entire volume of the gas. We have seen (on p. 104) that the work of expansion of the gas in this case will be maximum.

We would like to remind our readers once more that quasistatic processes may be depicted in the form of a curve showing how the pressure depends on the volume or, for example, how the pressure depends on the temperature. An irreversible process cannot be depicted by such a curve. If a process is non-equilibrium (not quasistatic), we cannot speak of a definite pressure or a definite temperature corresponding to the given value of the volume. All such naturally occurring processes as the transfer of heat from a hotter body to a colder one and the levelling out of the concentrations in gas mixtures are always irreversible and, naturally, non-quasistatic processes.

## 6.4. IRREVERSIBILITY AND PROBABILITY

We thus see that processes connected with the thermal movements of molecules differ from mechanical motion in that they are usually irreversible.

The movements of the molecules themselves, however, at least in a first approximation, obey the laws of mechanics, and we used these laws in deriving the basic equations of the kinetic theory of ideal gases. A natural question appears: how is it that a complex of particles each of which obeys the laws of mechanics, and the motion of which, consequently, is reversible, is capable only of irreversible changes (if we exclude quasistatic processes that do not occur by themselves)?

It will be now shown that the reason is the vastness of the number of the particles and the completely random nature of their movements. Let us

consider the following example to explain the cause of this qualitative difference appearing upon a quantitative change in the number of particles.

Assume that a vessel having the volume $V$ is filled with air. We shall mentally divide the volume of the vessel, for instance, into five parts each having the volume $V/5$ and introduce into one of them, say the bottom one distinguished by hatching (Fig. 91), one foreign molecule, for example a molecule of ether. Participating together with the air molecules in chaotic thermal movements, our molecule will soon leave the bottom part of the volume and in the course of its further motion will get into all five parts of the vessel, including the one which it has just left.

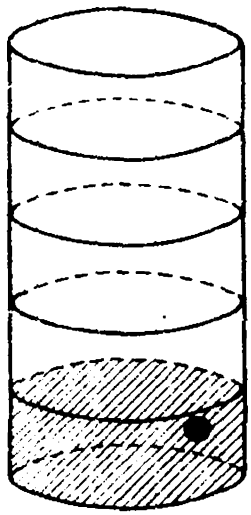


Fig. 91

If we are asked whether the transition of the ether molecule from the hatched volume $V'=V/5$ to the unhatched one is a reversible process, we shall have to answer that it is because without any external action our molecule will very soon again enter the part of the volume of the vessel it has left. And if we control its location every second, there is no doubt that in about one of every five observations we shall find it in the hatched volume $V'$. Using the concept of probability (see Sec. 1.10), we can say that the probability of finding a molecule in the volume $V'$ equals 1/5. This probability is sufficiently great to consider the process in question reversible, capable of proceeding in both directions.

If we now introduce two molecules of ether instead of one, the probability of their simultaneously being in volume $V'$, according to the theorem of multiplication of probabilities (the two molecules move independently of each other, and this is the reason why we use this theorem), equals $(1/5)^2$. This probability is already considerably smaller so that the process of the transition of the two molecules from the other parts of the volume $V$ into the hatched part $V'$ can be considered reversible with greater approximation. If we introduce 3, 4, 5, ... molecules of ether, the probability of again finding them all in the initial part of the volume will be, respectively, $(1/5)^3$, $(1/5)^4$, $(1/5)^5$, ... .

With a growth in the number of ether molecules originally introduced into $V'$, the probability of again finding them all there becomes smaller and smaller. Consequently, the natural process of mixing of the ether and air particles becomes less and less reversible.

This will become still more clear if we translate our reasoning into the language of time. Assume that one molecule leaving $V'$ returns there in 2 seconds. To wait for the return of not one, but two molecules, we need already $2^2$ s, of three molecules — $2^3$ s, etc. But if there are 100 ether molecules, then to observe the return of all the 100 molecules to $V'$, already $2^{100}$ s will be needed, and this is a number with over thirty digits that is a million times greater than the Earth's age. In nature, however, the number

of particles is generally not 100 and not 1000, but thousands and millions of millions. It is clear that the process of diffusion of one gas into another may be considered quite irreversible, although in principle a spontaneous reversible process is possible. But its probability is so small that it can be practically considered absolutely impossible.

Summarizing the above example, we can say that if a volume $V'$ equal to $1/m$ of the volume $V$ is separated from the latter, i.e. $V' = V/m$, then the probability $P$ of $N$ particles being in this separated part is $(1/m)^N$. If $N$ is great, the probability $P$ is very small.

Let us now imagine that in an empty vessel having the volume $V$ and deprived of a gas the volume $V' = V/m$ is set aside and separated from the remaining space by a partition. Let us introduce $N$ molecules of a gas into the volume $V'$ and remove the partition. It is quite obvious that after this all the particles of the gas will occupy the entire volume $V$. If the temperature is kept constant, this will be isothermal expansion of the gas from the volume $V'$ to the volume $V$. This expansion is a change in the state of the gas, and now we must already speak of a greater or smaller *probability of the state.*

In our case, we are dealing with a transition from the state when the gas is concentrated in the volume $V'$ (the state $V'$) to the state when it occupies the volume $V$ (the state $V$). We have already seen that the probability $P$ of the first of them equals $(1/m)^N$, or, since $m = V/V'$, we have

$$P = \left(\frac{V'}{V}\right)^N \tag{6.1}$$

As regards the state $V$, then since the gas can be nowhere except for the volume $V$ ($V'$ is also a part of $V$), the probability of this state equals unity. This can also be seen from Eq. (6.1) if we assume in it that $V' = V$.

The probabilities $P$ of states in which the gas concentrates in part of a volume instead of occupying it completely are exceedingly small at great values of $N$ (and the number of particles of a substance is virtually always great) even if $V'$ only slightly differs from $V$.

Let us calculate as an example the probability $P$ of the fact that a gas at atmospheric pressure and at room temperature ($T = 300$ K) will uniformly fill a vessel having a volume of $V = 1$ cm$^3$ except for $1/10^9$ of it. This means that

$$\frac{V - V'}{V} = 1 - \frac{V'}{V} = \alpha = 10^{-9}$$

The number of molecules

$$N = \frac{p}{kT} \approx 2.4 \times 10^{19}$$

hence, by Eq. (6.1), we have

$$P = \left(\frac{V'}{V}\right)^N = (1-\alpha)^N \tag{6.2}$$

Let us use a well-known formula for small values of $\alpha$ (in our case $\alpha = 10^{-9}$):

$$\lim_{\alpha \to 0} (1-\alpha)^{-1/\alpha} = e = 10^{\log e} = 10^{0.43}$$

(here $e$ is the base of natural logarithms). Equation (6.2) can therefore be transformed as follows:

$$P = \left(\frac{V'}{V}\right)^N = (1-\alpha)^N =$$

$$= \frac{1}{(1-\alpha)^{-\frac{1}{\alpha} N\alpha}} \approx \frac{1}{10^{0.43 \times 2.4 \times 10^{19} \times 10^{-9}}} \approx \frac{1}{10^{10^{10}}}$$

The number in the denominator of this fraction is one followed by ten thousand million zeroes. The probability of the fact that the molecules of the gas will gather in a volume forming a small part of the entire volume of the vessel is still lower. This is exactly the reason for the irreversibility of processes occurring naturally. If a gas spreads by itself throughout the entire volume of a vessel but never concentrates in a part of this volume, this does not mean that the latter of these processes is impossible in principle. On the contrary, the laws of mechanics which molecules obey permit both directions of the process, but owing to the great number of particles the probability of one of them is so small that it can virtually never be observed.

The above reasoning related to the particular case of the distribution of particles in a volume. But it can naturally be related to any other process in which particles participate in great numbers. The spontaneous concentration of molecules in a small part of the volume of a vessel has just as small a probability as the spontaneous transition of heat from a cold body to a hot one or the spontaneous separation of the components of a gas mixture. In all such cases, a transition to an equilibrium state whose probability is great occurs by itself. But the reverse transition to a non-equilibrium state does not virtually occur at all because the probability of such a state is small.

Hence, the irreversibility of processes in molecular systems consisting of particles each of which obeys the laws of mechanics, i.e. moves reversibly, is explained exclusively by the circumstance that the number of these particles is very great. If their number were small, a system would know no irreversible processes.

As regards quasistatic processes, then since the transition to equilibrium in these cases is performed through intermediate states that are also in equilibrium, they can proceed in either direction with an equal probability.

## 6.5. MUTUAL CONVERSIONS OF MECHANICAL AND HEAT ENERGY

The concepts of equilibrium, of reversibility and irreversibility of processes are general and relate to all processes in nature.

A process that often occurs in nature when a system is passing over to equilibrium is the conversion of mechanical energy into heat. An example of such a conversion is the liberation of heat in friction. We remind the reader that by mechanical energy here and in the following we mean macroscopic energy, i.e. the kinetic energy of motion of bodies and their potential energy due to the forces acting on these bodies. In contrast to this, the kinetic energy of the thermal movements of molecules and the potential energy of their interaction are called internal energy. Hence, the liberation of heat at the expense of mechanical energy is a process of conversion of macroscopic energy into the energy of microscopic thermal movements.

The reverse process is the conversion of heat into mechanical energy or, which is the same, the obtaining of mechanical energy at the expense of heat. At one time, the invention of methods of obtaining mechanical work at the expense of heat was the beginning of a new era in the history of civilization. Our time is the beginning of a no less important era of using nuclear energy for the obtaining of work. Nuclear energy too is not converted into mechanical work directly, however, but again through the agency of heat. This determines the importance of studying the general laws controlling the processes of the mutual conversion of mechanical and heat energy.

Historically, thermodynamics appeared as a branch of physics studying the relationships between mechanical and heat energy. Upon its further development, thermodynamics became a science studying the relationships between heat and all other kinds of energy—chemical, electrical, radiant, etc.

In the following sections we shall limit ourselves to a treatment of the general laws relating heat and mechanical energies.

## 6.6. THE FIRST LAW OF THERMODYNAMICS

The first law relating mechanical and heat energies is the law of conservation of energy which we have already considered in detail as applied to an ideal gas (see Sec. 2.4). It is exactly this law that is called the first law of thermodynamics. Let us remember the content of this law.

If the state of a system changes as a result of supplying a certain quantity of heat $dQ$ to it, and upon this change in state the system does the work $dW$, then the law of conservation of energy states that the quantity of supplied heat equals the sum of the work done and the change in the internal energy of the system. The law of conservation of energy is expressed mathematically as follows:

$$dQ = dU + dW \tag{6.3}$$

We have seen that

$$dW = p\,dV$$

Equation (6.3) can also be written in the form

$$dU = dQ - dW$$

If we are dealing with a macroscopic change in state instead of a small one, we must add up all the $dQ$'s and all the $dW$'s and thus calculate the change in the internal energy when the system passes over, for example, from state 1 to state 2:

$$\int_1^2 dU = \int_1^2 dQ - \int_1^2 dW$$

It is important to note here that the quantity of heat supplied, like the work done by the system (or on it), depends on how the system passed from state 1 to state 2. The change in the energy $dU$ is obviously independent of the path of the change and depends only on the initial and final states. We can therefore write that

$$\int_1^2 dU = U_2 - U_1 = \int_1^2 dQ - \int_1^2 dW$$

but we cannot write

$$\int_1^2 dQ = Q_2 - Q_1 \quad \text{or} \quad \int_1^2 dW = W_2 - W_1$$

This means that in each state a system has a definite value of the internal energy $U$, but we cannot say that it has a definite quantity of heat or work. The internal energy is therefore called a *function of state*. But $Q$ and $W$ are functions not of state, but of the *process* of a change in state. *

Of special importance are the so-called *cyclic* processes in which a system returns to its initial state after passing through a number of states. Here $\oint dU = 0$ (the sign $\oint$ stands for integration along a closed contour). But this does not at all mean that $Q$ and $W$ also equal zero. In a cyclic process, a body may receive or give up a certain quantity of heat, it may do work, or work may be done on it, but the change in the internal energy will equal zero.

*Mathematically, this means that unlike $dU$, the quantities $dQ$ and $dW$ are not total differentials.

In this case, the first law of thermodynamics is written as follows:

$$\oint dQ = \oint dW$$

The first law of thermodynamics is equally applicable to equilibrium and *non-equilibrium processes.* Although the latter cannot be represented in the form of a curve, the initial and final states of the system in this case too will be quite definite.

Let us remember here the main relationships which we obtained in applying the first law of thermodynamics to an ideal gas.

1. The work done by one mole of an ideal gas upon its isothermal expansion from the volume $V_1$ to the volume $V_2$ is

$$W = RT \ln \frac{V_2}{V_1} \tag{6.4}$$

2. In adiabatic expansion, if the temperature of a gas drops from $T_1$ to $T_2$, the work (related to one mole) done by a gas is

$$W = \frac{R(T_1 - T_2)}{\gamma - 1} \tag{6.5}$$

Here $\gamma = C_p/C_V$ is the ratio of the heat capacity at constant pressure to that at constant volume. It should be remembered that Eqs. (6.4) and (6.5) relate to the case when the change in the state of a gas is quasistatical, i.e. reversible.

It is important to note that the first law of thermodynamics does no indicate the direction in which the processes of the change in state occur. From the viewpoint of the first law, for instance, heat may pass either from a hot body to a cold one or from a cold body to a hot one. It is only essential that the energy given away by one body equal that received by the other one. The irreversibility of processes in nature does not follow, consequently, from the first law of thermodynamics.

The relationships given above permit us to calculate the quantity of heat liberated as a result of mechanical work. The result of mechanical work in definite cases may be the appearance of a quantity of heat equal to it. This means that the energy of macroscopic motion completely transforms into the energy of microscopic movements of the molecules of a substance.

Let us now consider the reverse process of the conversion of heat into mechanical work.

## 6.7. CONVERSION OF HEAT INTO MECHANICAL WORK

The energy transferred from a body with a higher temperature to one with a lower temperature, for example upon their contact, is called heat. In itself, such a transfer of energy is not attended by the performance of work because no bodies move during it. It results only in an increase in the internal energy of the body which heat is transferred to and in levelling out of the temperatures after which the process of heat transfer itself stops.

But if heat is transferred to a body which can expand, it can do work. According to the law of conservation of energy, this work equals

$$dW = dQ - dU$$

where $dU$ is the change in the internal energy. The maximum work is done in an isothermal process when the internal energy does not change so that

$$dW = dQ$$

More work cannot naturally be done. Therefore to obtain the maximum work equal to the supplied heat, we must transfer the heat to the expanding body so that there is no temperature difference between it and the source of heat. The reason is, we repeat, that an irreversible process of heat conductivity is useless for the conversion of heat into work and results only in an increase in the internal energy of a body to the detriment of work. True, if there is in general no temperature difference between the source of heat and the body which it is being transmitted to, no heat will be transferred. But an infinitely small temperature difference is sufficient for heat to be transferred, and this does not virtually differ from complete isothermality. The process of heat transfer proceeds infinitely slowly in such conditions and is therefore reversible.

All the above relates to a *single-fold* act of transferring heat to a body doing work. In this case, we repeat, the body can do work equal to the heat received from the source. For instance if a mole of an ideal gas upon receiving heat isothermally expands from the volume $V_1$ to the volume $V_2$, then work equal to $R \ln (V_2/V_1)$ will be done.

But it is not these single acts of conversion of heat into mechanical work that are of interest for engineering. The existing means for converting heat into work (steam engines, internal-combustion engines, etc.) function in *cycles*, i.e. the processes of the transfer of heat and its conversion into work in them periodically repeat. To this end, the body performing work after receiving heat from the source must return to the initial state so as to start the same process again. In other words, it must perform *cyclic processes*.

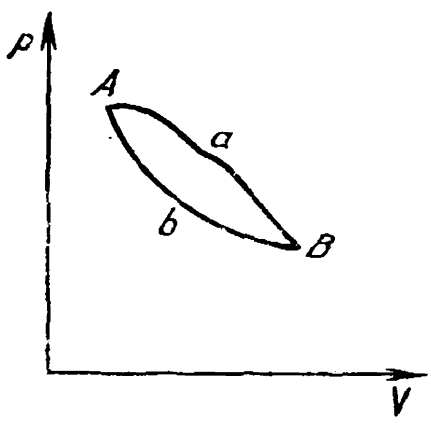



Fig. 92

A complex of the changes in state as a result of which the state is restored is called a *cycle*.

It should be remembered that if the state of a body is characterized by its pressure and volume, then this state will be depicted graphically by a point in a $p$-$V$ diagram. The changes in state will be shown by a line in such a diagram, for example by line $AaB$ in Fig. 92. A cyclic process (cycle) is depicted by a closed curve, for example by curve $AaBbA$. The work done during a cycle equals the area enveloped by this closed curve (see p. 102, Fig. 33).

**Kelvin's Principle.** An important question arises: is it possible even in a cyclic process to obtain work equal to the heat received from the source? At first sight, it seems that no obstacles will be encountered here. We know that as a result of a cycle the body doing work returns to its initial state, its internal energy remains unchanged, and the work ought to equal the absorbed heat. Actually, however, a complex of experimental data leads to a negative answer to the above question. It was formulated back in the last century (1854) by W. Thomson (Lord Kelvin) as the following general principle:

*It is impossible to conduct a cyclic process whose only result would be the conversion into mechanical work of the heat taken away from a body without any changes occurring in another body or bodies.*

According to this principle (based on numerous experimental data relating to the work of heat engines), the heat taken from the source can be converted into work in a cyclic process only provided that apart from this conversion the state of another body or bodies must change. Hence, in the process of converting heat into work in addition to the heat source from which the heat is taken away and the body doing work which the heat is directly transferred to, a third body (or bodies) must also participate. What is this "mysterious" body and what is its part in the process of the conversion of heat into work?

We have already learned that to convert heat into work we must "take away" heat from a source and transfer it to a body having a lower temperature. But such a transfer by itself is not connected with any work. It is therefore conducted not directly, but through another body that upon expanding performs "on its way" mechanical work and returns to its initial state. It is called the *working body*. The body heat is received from is called the *hot reservoir*, *heat source*, or *heater*, and the body with the lower temperature which heat is transferred to is called the *cold reservoir*, *heat sink*, or the *cooler*. It is exactly the latter that is the "other body" mentioned in Kelvin's principle. It itself does no work, but is needed because the working body must give up its heat to it.

The statement that the participation of two bodies with different temperatures is needed to perform work in a cyclic machine is called *Carnot's principle.*

But why didn't we need this additional body receiving heat but doing no work when we spoke of a single act of converting heat into work and why can't we do without it when speaking of a cyclic process?

The matter obviously is that in a cyclic process the working body after having expanded and done work at the expense of the heat received from the heat source must be returned to its initial state. If, for example, the working body in expanding and doing work passes through a number of states along curve *AaB* (see Fig. 92), it must be compressed for it to return to its initial state. And to do this, work must be performed on the working body. But this work must be less than that done by the working body in

expansion. Otherwise the object of our cycle will not be achieved. For the work in compression to be less than that of expansion, the working body in compression must pass through a number of states along a curve that is lower than the expansion curve, for instance along curve *BbA* in Fig. 92. But a lower curve in a $p$-$V$ diagram corresponds to a lower temperature. Hence, before compression, the working body must be cooled, a certain amount of heat must be taken away from it and transferred to the heat sink (cooler). This is why no heat engine (cyclic) can do only with a heat source and a working body.

If we could manage with only a working body and a heat source, we could obtain work by using such "sources" as the water of the seas and oceans, the Earth's crust, and the Earth's atmosphere from which we can take a virtually unlimited quantity of heat. An engine working at the expense of the heat of such a source and needing no fuel would have the same significance as a "perpetual motion machine" (such an imaginary machine is called a perpetual motion machine of the second kind). It is not "forbidden", however, by the law of conservation of energy — work is done at the expense of heat. But experiments show that such a machine can never be built. For the operation of a cyclic heat engine, we need a heat sink — a body having a lower temperature than that of the heat source. It is exactly the atmosphere that usually serves as the heat sink or cooler. We shall return to this question below.

## 6.8. THE CARNOT CYCLE

Let us now consider a cyclic process by means of which the heat taken away from a body can be converted into work, and this in the best possible way, i.e. so that the work obtained would be the maximum possible.

To carry out this process, we must have three bodies: a source of heat from which heat is taken away (a heater), a colder body which heat is transferred to (a heat sink or cooler), and a working body by means of which heat is transferred and work itself is done. Let us assume further that for simplicity of our reasoning the heat source and heat sink have such a great heat capacity that their temperatures do not change as a result of a certain quantity of heat being taken away from the former and transferred to the latter. Let us see how in such conditions the working body performs work at the expense of the heat imparted to it by the heat source.

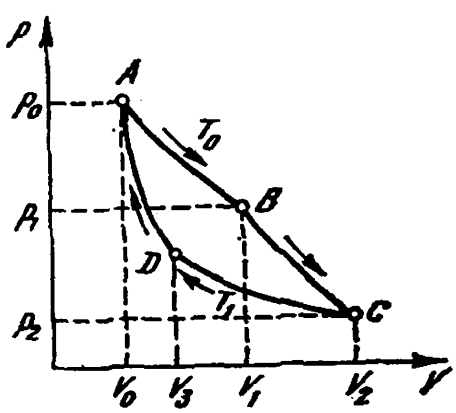


Fig. 93

We shall begin the cyclic process with the working body from the moment when it has been compressed to a certain pressure, is in contact with the heat source and, therefore, has the same

temperature $T_0$ as the latter (point $A$ in Fig. 93). No thermal conductivity occurs here because there is no temperature difference. Hence, there is no heat transfer without work being done. Since our task is to obtain the maximum work, we must not permit such processes in our cycle.

Let us now allow the working body to expand and move some other body, for example a piston, without interrupting its contact with the heat source. Expansion will therefore be isothermal (curve $AB$ in Fig. 93). Work will be done at the expense of the heat taken away from the source which, however, owing to its great heat capacity does not change its temperature.

The heat received by the working body must now be transferred to the heat sink. This transfer should also not be conducted by direct contact of the working body with the heat sink because the temperature of an isothermally expanding working body is higher than that of the sink, and the transfer of heat upon contact is not attended by the performance of useful work. Consequently, the working body must first be cooled to the temperature of the cooler, and only then may they be brought into contact. For cooling of the working body, it must be isolated from the heat source and then allowed to expand adiabatically (see curve $BC$ in Fig. 93) until it acquires the temperature of the heat sink (in adiabatic expansion a body cools). In this second stage, the body by expanding and moving, for instance, a piston additionally performs mechanical work. After the working body has been cooled in this way, it is brought into contact with the heat sink. This terminates the first half of the cycle during which the body performs useful work at the expense of the heat received from the heat source.

Now we must return the working body to its initial state, i.e. restore its initial pressure and temperature. This means that the working body must be compressed and again brought into contact with the heat source. As previously, this contact should not be allowed as long as the temperature of the working body is below that of the source. Therefore, the return to the initial state is also conducted in two stages. First, the working body is compressed without interrupting its contact with the cooler, i.e. isothermally (see curve $CD$ in Fig. 93). Next, after isolating the working body from the sink, it is additionally compressed adiabatically so that it becomes heated to the temperature of the heat source (see curve $DA$ in Fig. 93). In adiabatic compression, a body becomes heated at the expense of the external work done on it. After the temperature of the working body has become equal to that of the heat source in the process of adiabatic compression, they are brought into contact, and the cycle is completed — the working body is in its initial state, and the process can be started once more.

The above cyclic process thus consists of two isothermal and two adiabatic expansions and compressions. During the expansions, the working body performs useful work; the compressions, on the contrary, proceed at the expense of the work done on the working body by external forces.

At all stages of the cyclic process considered, no contact is permitted between two bodies with different temperatures, and thus the appearance of

an irreversible thermal conductivity process is avoided. The entire cycle is conducted, consequently, reversibly (for complete reversibility the expansions and compressions must be conducted very slowly, in principle infinitely slowly so that these processes will be quasistatic).

The cycle described above performed by a working body is called the *Carnot cycle* after the French scientist Sadi Carnot who was the first to consider it.

As a result of a Carnot cycle, a certain quantity of heat is transferred from the heat source to the heat sink by means of the working body. Apart from this, in the course of the process the working body does some work. Work is done on the working body, in turn, by external forces. Is useful mechanical work obtained here, i.e. is the object of the entire process achieved?

At first sight, the work done by the working body upon its expansion in the first two stages of the cycle seems to be completely compensated by the work done by external forces in the following two cycles so that the useful work in the long run equals zero. Actually, however, it is not difficult to see that the positive work done by a body upon its expansion is greater than the negative work done on it upon its compression and that, consequently, part of the heat received from the heat source is actually converted into mechanical work.

It is the simplest to see that this is true in the case when the working body is an ideal gas for which we can accurately calculate the work of expansion and compression. We shall see that the conclusions we arrive at do not depend on the nature of the working body, i.e. hold for any body.

Let us therefore quantitatively consider the entire Carnot cycle when an ideal gas is the working body (see Fig. 93).

Suppose that one mole of an ideal gas is the working body and that the initial state is characterized by the pressure $p_0$ and the volume $V_0$, i.e. by point $A$ in Fig. 93. The temperature of the gas $T_0 = p_0V_0/R$ according to our condition equals the temperature of the heat source. Let $T_1$ stand for the temperature of the heat sink. Hence, $T_0 > T_1$.

In the initial state, the working body is in contact with the source. The first stage of the cyclic process performed by the gas is isothermal expansion (contact with the source is retained) to the volume $V_1$. The pressure correspondingly drops along an isotherm to the value $p_1$ (point $B$ in Fig. 93).

The positive work done by the gas in expansion equals

$$W_1 = RT_0 \ln \frac{V_1}{V_0} = Q_0 \tag{6.6}$$

where $Q_0$ is the quantity of heat received by the gas from the heat source. The work $W_1$ is done at the expense of this heat.

The second stage consists in isolation of the gas from the heat source and its further adiabatic expansion, as a result of which the gas cools. This adiabatic expansion stops when the temperature of the gas becomes

equal to that of the heat sink $T_1$. The value of the volume which the gas must expand to can be determined with a view to the fact that the equation

$$T_0 V_1^{\gamma-1} = T_1 V_2^{\gamma-1} \tag{6.7}$$

holds for adiabatic expansion. Hence, the volume $V_2$ can be found from the equation

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_0}{T_1} \tag{6.8}$$

The pressure here changes along an adiabatic curve to the value $p_2$ (point $C$ in Fig. 93). The work done by the gas in this second stage of the process is (see p. 123)

$$W_2 = \frac{RT_0}{\gamma-1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] = \frac{R(T_0 - T_1)}{\gamma - 1} \tag{6.9}$$

In the third stage of the cyclic process, the gas is isothermally compressed by external forces at the temperature $T_1$ of the heat sink from the volume $V_2$ to $V_3$. The work done *on the gas* here is

$$W_3 = RT_1 \ln \frac{V_3}{V_2} = -RT_1 \ln \frac{V_2}{V_3} = Q_1 \tag{6.10}$$

At the expense of this work, the heat $Q_1$ is liberated and transferred to the heat sink which the gas is in contact with.

Finally, the last change which the gas undergoes to return to its initial state is adiabatic compression to the initial volume $V_0$ and pressure $p_0$ at which its temperature becomes equal to $T_0$. For this purpose, it is essential that the gas in the preceding third stage be compressed to the volume $V_3$ determined by the equation

$$\left(\frac{V_3}{V_0}\right)^{\gamma-1} = \frac{T_0}{T_1} \tag{6.11}$$

because as previously $T_1 V_3^{\gamma-1} = T_0 V_0^{\gamma-1}$.

The work of compression in the last stage of the cycle is

$$W_4 = \frac{R(T_1 - T_0)}{\gamma - 1} = -\frac{R(T_0 - T_1)}{\gamma - 1} \tag{6.12}$$

Now the gas is again in its initial state, the Carnot cycle is completed, and the gas is "ready" to again begin the process.

What is the result of the cycle? To what extent has its object been achieved — the conversion of heat into mechanical work?

The total work $W$ done by the gas and on the gas obviously equals

$$W = W_1 + W_2 + W_3 + W_4$$

From Eqs. (6.6), (6.9), (6.10), and (6.12), we get:

$$W = RT_0 \ln \frac{V_1}{V_0} + \frac{R(T_0 - T_1)}{\gamma - 1} - RT_1 \ln \frac{V_2}{V_3} - \frac{R(T_0 - T_1)}{\gamma - 1} =$$

$$= RT_0 \ln \frac{V_1}{V_0} - RT_1 \ln \frac{V_2}{V_3}$$

It follows from Eqs. (6.8) and (6.11) that $V_2/V_1 = V_3/V_0$, or $V_1/V_0 = V_2/V_3$. Let us denote this ratio by $r$. Hence,

$$\ln \frac{V_1}{V_0} = \ln \frac{V_2}{V_3} = \ln r \tag{6.13}$$

Since $V_1 > V_0$ and $V_2 > V_3$, then $\ln r > 0$.

Consequently, the total work is

$$W = R(T_0 - T_1) \ln r \tag{6.14}$$

This work is greater than zero because $T_0 > T_1$. Therefore, the work done by the gas upon expansion is greater than the work of the external forces spent for its compression. Thus, a certain amount of useful work has been done at the expense of the heat received by the working body from the heat source. This work, however, does not equal the quantity of heat $Q_0$ that the working body received from the heat source.

Of the quantity of heat given away by the heat source, i.e.

$$Q_0 = RT_0 \ln \frac{V_1}{V_0}$$

a part equal to

$$Q_1 = RT_1 \ln \frac{V_3}{V_2}$$

was transferred to the heat sink upon isothermal compression of the gas from the volume $V_2$ to the volume $V_3$ (the gas at this time was in contact with the heat sink). Thus, it was found possible to convert only a part of the heat received, i.e.

$$Q_0 - Q_1 = R(T_0 - T_1) \ln r = W \tag{6.15}$$

into useful work. The work $W$ is graphically determined by the area bounded by curve *ABCDA* (see Fig. 93).

This is the difference between the process of converting heat into work and the reverse process of converting work into heat. Mechanical work can be completely converted into heat in definite conditions. Heat is only partly converted into work.

We must note here that Eqs. (6.6), (6.10), and (6.13) yield a very important relationship which we shall need in the future.

Equations (6.6) and (6.10) can be rewritten in the form

$$\frac{Q_0}{T_0} = R \ln \frac{V_1}{V_0}, \quad -\frac{Q_1}{T_1} = R \ln \frac{V_2}{V_3}$$

By summating them and taking into consideration Eq. (6.13), we get $Q_0/T_0 - Q_1/T_1 = 0$, whence

$$\frac{Q_0}{T_0} = \frac{Q_1}{T_1} \tag{6.16}$$

**Efficiency in the Carnot Cycle.** The above analysis of the Carnot cyclic process shows that it cannot be used to completely convert heat taken from a heat source into mechanical energy. Part of this heat must be given up without fail to a heat sink — a body having a lower temperature than the heat source.

If the quantity of heat received by the working body from the heat source is $Q_0$, and its part $Q_0 - Q_1$ is transformed into work, then the ratio

$$\eta = \frac{Q_0 - Q_1}{Q_0} \tag{6.17}$$

is the *efficiency* of the cyclic process (more exactly of a machine working according to this process). A glance at Eq. (6.16) shows that the efficiency $\eta$ of the Carnot cycle is determined by the equation

$$\eta = \frac{Q_0 - Q_1}{Q_0} = 1 - \frac{Q_1}{Q_0} = 1 - \frac{T_1}{T_0} \tag{6.18}$$

The efficiency is consequently always less than unity and depends on the ratio between the temperatures of the heat source and heat sink.

The Carnot cycle which we have considered was so conducted in all its stages that nowhere bodies with different temperatures came into contact. This excludes the possibility of irreversible thermal conductivity processes. The changes in the volume of the working body were also conducted reversibly which, as we know, ensures the maximum work being performed (see Sec. 2.4). This means that the best conditions were ensured for the utilization of heat energy. Therefore, it is impossible in principle to obtain a higher efficiency than that given by Eq. (6.18).

*A heat engine working at given values of the temperatures of the heat source and the heat sink cannot have a greater efficiency than an engine working according to the reversible Carnot cycle at the same values of the temperatures of the heat source and the heat sink.* (This statement is sometimes called *Carnot's first theorem.*)

Inspection of Eq. (6.18) shows that *the efficiency of a Carnot cycle does not depend on the kind of the working body, but depends only on the temperatures of the heat source and the heat sink.* (This statement is called *Carnot's second theorem.*)

In our calculations, we selected an ideal gas as the working body because the equation of state is known for it. This made it easy for us to calculate the efficiency.

The circumstance that the efficiency of a machine working according to the Carnot cycle is maximum is due, as we have seen (and will see in greater detail below), to this cyclic process being completely reversible. General proofs of both Carnot's theorems will be given in Sec. 6.10.

## 6.9. REFRIGERATING MACHINE

We have already pointed out that a reversible process is characterized by the fact that if it is conducted in the reverse direction, the body participating in the process will pass through the same states, but in the reverse sequence. As applied to the Carnot cycle, this means that heat will be transmitted not from the heat source to the heat sink, but in the opposite direction — from the sink to the source.

The inverted Carnot cycle begins with the working body being, for example, in a state corresponding to point $A$ (Fig. 94). It adiabatically expands to a state corresponding to point $D$ (in the direct cycle the process begins with isothermal expansion). Next comes isothermal expansion to state $C$. In these first two stages of the cycle, the working body expands and does work. In the second half of the cycle — along adiabat $CB$ and isotherm $BA$ — the working body compresses, and the work of compression is performed on the body by an external source of energy. We have just shown that this work exceeds the work done by the body itself during the first half of the cycle. Therefore, the result of the inverted Carnot cycle (also called the Carnot refrigerating cycle) will be not external useful work, but the transfer of heat from the heat sink to the heat source, i.e. from a colder body to a warmer one.

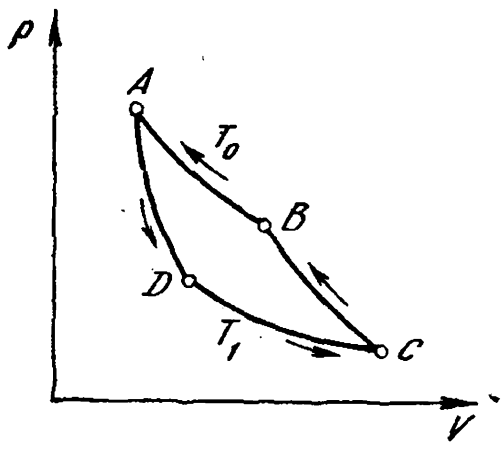


Fig. 94

It is not difficult to see that in the inverted Carnot cycle the working body passes through the same intermediate states as in the direct one, but in the reverse order.

If a machine operating according to the direct Carnot cycle converts heat into mechanical work, i.e. is a *heat engine*, then a machine operating according to the inverted Carnot cycle is used for transferring heat from a colder body to a warmer one, i.e. is a *refrigerating machine*. With its aid, heat is taken away from a colder body and transferred to a warmer body at the expense of external mechanical work.

## 6.10. PROOF OF CARNOT'S THEOREMS

Now we can give a stricter proof of *Carnot's first theorem*, which can be formulated as follows: *the efficiency of a heat engine working at given values of the temperatures of the heat source and the heat sink cannot be greater than that of a machine working according to a reversible Carnot cycle at the same values of the temperatures of the heat source and the heat sink.*

Suppose we have two heat engines with a *common* heat source and heat sink: engine *I* working according to a reversible Carnot cycle and engine *II* differing from *I* either in the irreversibility of processes in it or in the kind of the working substance. Let us first assume that the efficiency $\eta_2$ of machine *II* is greater than the efficiency $\eta_1$ of machine *I*:

$$\eta_2 > \eta_1$$

Let us connect our engines (by means of a common shaft, a belt transmission or the like) so that one of them can drive the other. Assume that engine *II* works according to the direct cycle, i.e. receives the heat $Q_0$ from the heat source, does the work $W_2$, and transfers to the heat sink a quantity of heat equal to $Q_0 - W_2$.

It drives engine *I* so that the latter performs an inverted cycle, i.e. operates like a refrigerating machine. Hence, engine *I* at the expense of the work done on it by engine *II* transfers heat from the heat sink to the heat source. Assume that engine *I* transmits to the source in each cycle the quantity of heat $Q_0$, i.e. the same quantity that is absorbed during one cycle by engine *II*. Let the work needed for this be $W_1$. Therefore, the heat taken away by engine *I* from the heat sink equals $Q_0 - W_1$.

After one cycle in the combined engine *I-II*, we get the following result.

1. The heat source underwent no changes because engine *I* transferred to it the same quantity of heat that was taken away from it by engine *II*.

2. The working body in each engine returned to its initial state after performing a cyclic process, i.e. also experienced no changes.

3. The heat sink received the heat $Q_0 - W_2$ from engine *II* and gave up the heat $Q_0 - W_1$ to engine *I*. Since according to our assumption, $\eta_2 > \eta_1$, then $W_2 > W_1$, and

$$Q_0 - W_1 > Q_0 - W_2$$

This means that the only result of the entire cycle was the extraction from the heat sink of a quantity of heat equal to $W_2 - W_1$ and the conversion of it into work. But this contradicts Thomson's principle. Consequently, $\eta_2$ cannot be greater than the efficiency $\eta_1$ of a reversible Carnot machine.

We shall now prove the truth of *Carnot's second theorem* that *the efficiency of a reversible Carnot machine does not depend on the nature of the working body.* Let us again take two heat engines *I* and *II* connected to-

gether and having a common heat source and heat sink. This time both engines work according to a reversible Carnot cycle and differ from each other only in their working substances. We shall prove that the efficiencies of both engines $\eta_1$ and $\eta_2$ are equal. Let us assume again that engine *II* performs a direct cycle and engine *I* an inverted one. Let us first assume that the efficiencies of both engines differ, and that, for example, $\eta_1 < \eta_2$.

In performing the direct cycle, engine *II* receives from the heat source the quantity of heat $Q_1$, gives up to the heat sink the heat $Q_2$, and performs work equivalent to $Q_1 - Q_2$. Engine *I*, performing the inverted cycle, takes away from the heat sink the heat $Q_0$ and gives up the heat $Q_1$ to the heat source at the expense of mechanical work equivalent to $Q_0 - Q_1$. If the efficiency $\eta_1 < \eta_2$, then $Q_0 > Q_2$.

The heat difference $Q_0 - Q_2$ is converted into work. Hence, as a result of the cycle, the heat source undergoes no changes because it receives from one engine the same quantity of heat that it gives away to the other. The working bodies will also be in their initial state after completing a cyclic process. Hence, the only result of the cycle is the removal of heat (amounting to $Q_0 - Q_2$) from the heat sink and its conversion into work, which contradicts Thomson's principle. Consequently, the assumption that $\eta_1 < \eta_2$ is wrong.

Let us now change the order of operation of the engines, i.e. assume that engine *I* performs a direct cycle and engine *II* an inverted one. By using the same reasoning, we find that the assumption that $\eta_1 > \eta_2$ is also wrong. Therefore, the only remaining possibility is that $\eta_1 = \eta_2$.

Since the working body in one of the engines may be an ideal gas, and we have already shown that for this case $\eta = (T_0 - T_1)/T_0$, where $T_1$ and $T_0$ are the temperatures of the heat sink and the heat source, respectively, it follows that for any *reversible* Carnot machine the efficiency will be the same. For an *irreversible* cycle, the efficiency

$$\eta < \frac{T_0 - T_1}{T_0} \tag{6.19}$$

It should be remembered [see Eq. (6.17)] that

$$\eta = \frac{Q_0 - Q_1}{Q_0}$$

where $Q_0$ = quantity of heat given away (to the working body) by the heat source

$Q_1$ = quantity of heat received (from the working body) by the heat sink.

But if we consider our process from the viewpoint of the changes occurring *in the working body itself,* then $Q_0$ and $Q_1$ are the quantities of heat *received* and correspondingly *given away* by the working body. These quantities $Q_0$ and $Q_1$ should obviously be given *opposite signs.*

We shall consider that the quantity of heat $Q_0$ received by the body is positive; hence $Q_1$ is negative.

Consequently, inequality (6.19) can be rewritten in the form

$$\frac{Q_0 + Q_1}{Q_0} < \frac{T_0 - T_1}{T_0}$$

or

$$\frac{Q_0}{T_0} + \frac{Q_1}{T_1} < 0 \tag{6.20}$$

It is evident [see Eq. (6.16)] that if a body is subjected to a reversible process, then

$$\frac{Q_0}{T_0} + \frac{Q_1}{T_1} = 0 \tag{6.21}$$

Expressions (6.20) and (6.21) will be generalized somewhat later.

It is clear from the above what has to be done to achieve the highest possible efficiency of a heat engine. First, irreversible processes should be excluded as much as possible so that the cycle of the engine would be as close as possible to a reversible one.

Second, the temperature of the heat source should be raised and that of the heat sink lowered as far as possible [see Eq. (6.18)].

As regards the choice of the working body, it is dictated by considerations of technical and economical expediency. The circumstance that steam is used in modern heat engines to a great extent is due to the availability of water and the simplicity of handling it.

Progress in steam-power plants is achieved by increasing the temperature of the heat source (the surrounding air is usually the heat sink). But internal-combustion engines, in which air mixed with the corresponding fuel is the working body, are successfully competing with steam-power plants. The temperatures reached in this case are considerably higher, and, therefore, the efficiency of the internal-combustion engines is greater. In addition, the latter engines do without the irreversible process of transferring heat from a furnace, which also increases their efficiency.

It must be borne in mind, however, that a reversible process is ideal, and in practice complete reversibility cannot be achieved. Therefore, the value of the efficiency of a heat engine given by Eq. (6.18) is actually an unattainable upper limit which in principle, however, can be approached infinitely closely.

## 6.11. FREE ENERGY

In a Carnot cycle, the working body does work in the first half of the cycle — first in an isothermal and then in an adiabatic processes of expansion.

In an adiabatic process, work is done at the expense of the internal energy, and this work is exactly equal to the decrease in the internal energy:

$$dW = -dU$$

Matters are different in an isothermal process. In the latter, the temperature of the body remains constant, and therefore the part of the internal energy that is connected with the kinetic energy of molecular movements cannot be used for conversion into mechanical energy. This circumstance makes us distinguish between the total energy which a body or a system of bodies has and the part of it that in the given conditions can be used for obtaining work.

Imagine a certain body, for instance a gas, in which *isothermal reversible* processes of expansion and compression can occur. For this purpose, the gas must be placed in a thermostat (see Sec. 2.9), i.e. brought into contact with a body having a great heat capacity whose temperature is constant. The gas upon expanding can perform mechanical work, hence our system consisting of a thermostat and a gas has a certain energy. The part of the energy of a system that in given conditions can be used for conversion into mechanical work is called *free energy*.

This means that a system cannot do work exceeding the value of its free energy.

In this sense, we have a situation here that differs somewhat from a mechanical system. In mechanics, we know that the energy of a body or a system of bodies equals the sum of the potential and kinetic energies. Both these kinds of energy of macroscopic bodies (and only such bodies are considered in mechanics) can be *completely* converted into mechanical work. The internal energy of a molecular system, however, in the case we are interested in cannot be completely converted into work.

Hence, if we are interested in the magnitude of the work which a system in the given state can perform in an isothermal process, the internal energy is not a suitable characteristic of this state. The internal energy characterizes the state of a system if we are interested in the work which this system can do in an *adiabatic* process, namely, the work done in an adiabatic process equals the change (diminishing) in the internal energy. The free energy, however, should characterize a system from the viewpoint of its "workability" upon an *isothermal* change in its state (a change in volume).

To be able to assign a definite numerical value of the free energy to each state, we must take an arbitrary state as the beginning of counting (the "datum level") as is done in determining the value of potential energy in mechanics. This indeterminacy of the absolute value of the free energy creates no difficulties because it is not the value of the free energy itself of a system that is of importance, but its *change*. The work done is determined by the latter. We must also remember that the work of expansion or compression of a body has a definite value if the process goes on in equilibrium, i.e. quasistatically.

Thus, *the free energy of a system is measured by the work which the system (for instance an ideal gas) can do in changing its state isothermally and reversibly from the state it is in to the initial state we have selected at which the free energy is assumed to equal zero (the datum point).*

If we denote the free energy of a system by $A$, then the infinitely small work $dW$ done by the system in a reversible isothermal process is

$$dW = -dA \tag{6.22}$$

If, for example, a change in the state of a system consists in the isothermal expansion of a body (an increase in its volume) when the work done is positive, the minus sign indicates that here the free energy diminishes. Conversely, when a body is compressed (the work is negative), the free energy grows at the expense of the external forces compressing the body (gas). In particular, for an ideal gas upon its isothermal expansion from the volume $V_1$ to the volume $V_2$, the work is known to be expressed by the equation (for one mole)

$$W = RT \ln \frac{V_2}{V_1} \tag{6.23}$$

The right-hand side of Eq. (6.23) is the decrease in the free energy of one mole of a gas in such expansion. This means that at the given temperature the free energy of a given mass of the gas is the greater, the smaller is the volume it occupies, i.e. the more it is compressed.

It should be remembered that the *internal* energy of an ideal gas *does not depend* on the volume it occupies; one mole of a gas compressed in a cylinder has the same internal energy as an uncompressed gas at the same temperature. But the compressed gas has a greater *free energy* because in isothermal expansion it can do more work.

When this compressed gas actually performs work upon isothermal expansion (lifting, for example, a piston with a weight), the work is done at the expense of the heat that should be supplied to the gas from a thermostat or some other body having a very great heat capacity (otherwise the gas will cool, and the process will not be isothermal). But we nevertheless speak of the free energy of the *gas* because we want to stress that the gas is the body owing to which the possibility of doing work is created.

If the process of the isothermal change in volume proceeds irreversibly, then since the work done is less (see p. 104) than in a reversible process, the change in the free energy will be greater than the work done so that Eq. (6.22) should be written in the form

$$dW \leqslant dA$$

The inequality sign relates to an irreversible, and the equality sign to a reversible process.

Cases are also possible when the change in the free energy is in general not attended by the performance of work.

Particularly, if an ideal gas expands into a vacuum, no work is performed in the process. The temperature and, consequently, the internal energy of the gas remain constant. But the free energy of the gas *diminished* because the work which the gas *can* do decreased. This is connected with the fact

that the process of expansion of a gas into a vacuum, although being isothermal, is completely *irreversible*.

At the beginning of this section, we underlined that the free energy characterizes the *state* of a body. It remains for us to prove that it actually is a function of state, i.e. to prove that when a body is transferred from one state to another isothermally and reversibly, the work done equal to the difference between the free energies of the body in these states does not depend on the path followed during this transfer. This directly follows from the fact that in an isothermal reversible *cyclic* process the work equals zero.

Indeed, assume that a body can pass from state *1* to state *2* along two different paths (isothermal) doing the work $W_1$ along the first path and the work $W_2'$ along the second. But in this case we can transfer our body from state *1* to state *2* along one path and return it along another one, completing a cyclic process. The total work done is $W_1 - W_2 = 0$, and, therefore, $W_1' = W_2$.

This means that the work done by a body depends only on its initial and final states. Therefore, the free energy is a *function of state*.

A general formula for the free energy will be given in a following section (see p. 287).

## 6.12. ENTROPY

Let us return to the Carnot cycle we have already considered and give greater attention to the changes in state which the *working body* experienced in this cycle.

We shall remind the reader that from initial state $A$ characterized by the pressure $p_0$ and temperature $T_0$, the working body as a result of sequential isothermal and adiabatic expansions passed to state $C$ when it acquired the temperature of the heat sink. This change in state occurred at the expense of the heat $Q_0$ supplied to the working body by the heat source. The reverse transition of the working body from state $C$ to initial state $A$ was achieved by sequential isothermal and adiabatic compressions of the body. The quantity of heat liberated during this return to the initial state equals $Q_1$, and we saw that $Q_1 < Q_0$. We can thus see that the reversible transition of the same body from state $A$ to state $C$ and the reverse transition from $C$ to $A$ are attended by different quantities of absorbed and liberated heat. This is evidently connected with the fact that the two transitions were performed along different paths: in one case (from $A$ to $C$) the expansion process was conducted at a higher pressure than the compression processes in the other (from $C$ to $A$). It is clear that if we conducted the transition from $C$ to $A$ in the same way as the forward transition, i.e. along curve $CBA$ instead of $CDA$ (see Fig. 93), the quantity of heat spent in the forward transition would exactly equal the quantity liberated in the reverse transition.

Hence follows an important conclusion which we have already attracted our readers' attention to that the quantity of heat to be supplied to a body or taken away from it when it passes from one state to another is not determined unambiguously by the initial and final states, but appreciably depends on how this transition is conducted. In other words, the quantity of heat $Q$ is not a function of state of a body as, for example, the internal energy $U$ (or the free energy $A$) is. This follows from the equation of the first law of thermodynamics

$$dQ = dU + dW$$

because the work $dW$ done by a body (or on the body) depends on its path, whereas the change in the internal energy $dU$ does not depend on how the change in state occurred.

But if the quantities of heat $-Q_0$ supplied to the body from the heat source at the temperature $T_0$, and $Q_1$ transmitted to it by the heat sink at the temperature $T_1$ — do not themselves equal each other, then, as we have seen [see Eq. (6.16)], the ratios of these heats to the temperatures at which they were absorbed or given away are numerically equal to each other (but have opposite signs):

$$\left|\frac{Q_0}{T_0}\right| = \left|\frac{Q_1}{T_1}\right| \tag{6.24}$$

H. Lorentz proposed to call the ratio $Q/T$ the *reduced heat* so that Eq. (6.24) indicates the equality of the reduced heats received and given up by the working body in a cyclic process.

This feature of heat permits us to introduce a special thermodynamic quantity — the *entropy*, which has a fundamental significance in physics. The importance of this quantity is determined by the circumstance that, as will be shown below, it is a *function of state*, and by the part it plays in all processes in nature, particularly in the process of the conversion of heat into work. *

Any change in the state of a body or a system of bodies can be represented in the general case as the result of an infinitely great number of infinitely small changes. In every such infinitely small change in state, a system either absorbs or liberates an infinitely small quantity of heat $dQ$ (if the process is not adiabatic). Let us assume that $dQ$ is positive when a system absorbs heat, and negative when it liberates heat.

---

*The word "entropy" itself comes from the Greek verb εντρεπειν meaning to convert, to transform, and was proposed by R. Clausius, one of the founders of thermodynamics.

It can be shown that if a system as a result of changes in state reversibly passes from state $A$ to state $B$, the sum of the reduced quantities of heat, i.e. the quantity

$$\int_A^B \frac{dQ}{T}$$

does not depend on the path along which the transition from $A$ to $B$ occurs. For this purpose, it is sufficient to prove that in a cyclic process, when the initial and final states coincide, this integral equals zero:

$$\oint \frac{dQ}{T} = 0$$

We shall first prove that in any cyclic process the integral

$$\oint \frac{dQ}{T} \tag{6.25}$$

cannot be a positive quantity.

Suppose that a certain body $M$ as a result of changes in its state returns to its initial state, i.e. performs a cyclic process. During the process, the body gave up and absorbed heat. Imagine that the heat liberated by body $M$ is transmitted to a heat reservoir (a body having a great heat capacity) whose temperature is $T_0$. This transfer can be conducted reversibly, for instance with the aid of an intermediate body performing a Carnot cycle so that body $M$ will serve as a heat source for the intermediate body, and the reservoir as a heat sink.

We have already seen in considering the Carnot cycle that the quantity of heat $dQ$ taken away from body $M$ at the temperature $T$, and the quantity of heat $dQ'$ transmitted to the reservoir at the temperature $T_0$ do not equal each other, but the ratios $dQ/T$ and $dQ'/T_0$ are equal. Hence it follows that

$$dQ' = \frac{T_0}{T} dQ \tag{6.26}$$

If $T_0 < T$, the reservoir plays the part of a heat sink, and body $M$ of a heat source. If, conversely, $T_0 > T$, the reservoir and body $M$ exchange the parts they play.

After body $M$ completes a cyclic process, the total quantity of heat lost by the body should equal, as can be seen from Eq. (6.26),

$$\oint T_0 \frac{dQ}{T}$$

or, since the heat capacity of the reservoir is great and its temperature therefore remains constant, this quantity equals

$$T_0 \oint \frac{dQ}{T}$$

The process completed by the body is a cyclic one. Therefore, in the long run it underwent no changes. The intermediate body also experienced no changes because it completed a cyclic process too.

If integral (6.25) were positive, this would mean that the quantity of heat lost by the body and equal to $T_0 \oint \frac{dQ}{T}$ was completely converted into work whereas neither body $M$ nor the intermediate body changed their state. But this is impossible according to Thomson's principle. Hence, the assumption that $\oint \frac{dQ}{T} > 0$ is groundless.

It is easy to see that integral (6.25) also cannot be negative. Indeed, if all the changes in state are conducted in the reverse sequence, then each quantity of heat will change its sign, and if in the forward process $\oint \frac{dQ}{T} < 0$, then in the reverse one this integral will become positive, which as we have just seen is impossible. Therefore, this integral also cannot be negative. But if it can be neither positive nor negative, this means that for *reversible cyclic* processes which we are considering here we have

$$\oint \frac{dQ}{T} = 0 \tag{6.27}$$

[Equation (6.21) is a particular case of this equation.]

This means, in turn, that for any *reversible non-cyclic* process the value of $\int \frac{dQ}{T}$ *does not depend on the path* along which the process is conducted.

This gives us the right to state that there is a certain quantity — let us denote it by the letter $S$ — that is a function of state of a system whose change $S_B - S_A$ in a reversible transition of the system from state $A$ to state $B$ equals

$$S_B - S_A = \int_A^B \frac{dQ}{T} \tag{6.28}$$

Equation (6.28) permits us to determine not the absolute value of the function corresponding to the given state, but only its change upon a transition from one state to another. As is always done in such cases, however, we can choose a certain state which a value of $S$ equal to zero is ascribed to and compare all other states with it. We shall therefore con-

sider in the following that it is the function $S$ which is equal to integral (6.25):

$$S = \int \frac{dQ}{T} \tag{6.29}$$

The quantity $S$ determined in this way is called the *entropy*.

In practice, we must always know not the quantity $S$ itself, but only its change when the state of a system changes. It therefore makes no difference what state we assign a zero entropy to. The entropy is conventionally considered to equal zero at the absolute zero of the temperature (and there are sufficient grounds for this).

Hence, to find the entropy of a system in a given state, we have to transfer the system (this can be done mentally (from this state to the zero one along a *reversible* path (it makes no difference along which path) and find the value of $\int \frac{dQ}{T}$ along it. Naturally, the entropy of the system does not depend at all on whether or not this reversible process is conducted.

The same relates to the change in entropy. According to Eq. (6.28), to determine the difference between the values of the entropy of a system in two (equilibrium) states $A$ and $B$ of it, we must transfer the system using *any* reversible process from state $A$ to state $B$ and calculate the value of $\int_A^B \frac{dQ}{T}$ for such a process.

The change in the entropy of a system which an infinitely small amount of heat $dQ$ has been supplied to is obviously determined by the relationship

$$dS = \frac{dQ}{T} \tag{6.30}$$

In a mathematical respect, this equation is interesting in that the quantity $dQ$ which is not a total differential because $Q$ is not a function of state (see the footnote on p. 252) does become a total differential after being divided by $T$. The quantity $1/T$ is thus an integrating factor for $dQ$. From the mathematical viewpoint, the temperature can formally even be defined as a quantity whose reciprocal is an integrating factor for $dQ$.

Using Eq. (6.30) and remembering that $dQ = dU + dW$ (the first law of thermodynamics), we get

$$T\,dS \equiv dU + dW \tag{6.31}$$

This equation is called a *thermodynamic identity*. It is often called the second law of thermodynamics for *reversible processes*.

Properly speaking, the second law of thermodynamics for reversible processes consists in that a system can be characterized by a function of state — entropy which is determined by Eq. (6.30) or (6.31). The profound physical meaning of this function will be explained below.

If a cyclic process which a system is subjected to is *irreversible*, then

$$\oint \frac{dQ}{T} < 0 \tag{6.32}$$

This inequality is called the *Clausius inequality*.

For the particular case of an irreversible Carnot cycle, we have already seen [see expression (6.20)] that the sum of the reduced heats

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0 \tag{6.33}$$

Inequality (6.32) is a generalization of (6.33) for any system. We send the reader to special courses in thermodynamics for a strict proof of this inequality.

In the same way, Eq. (6.27) is a generalization of Eq. (6.21).

## 6.13. SOME THERMODYNAMIC RELATIONSHIPS

Entropy, being a function of state of a body or a system of bodies, can serve as the same parameter of state of a body (for instance a gas) as the quantities we already know: the temperature $T$, pressure $p$, and volume $V$.

In the same way as any of these quantities is a function of the other two, the entropy can be expressed through any two of the parameters $p$, $V$, and $T$. Let us see how this can be done. This is very important because the entropy cannot be measured directly by experiments like the temperature, volume, or pressure, for example.

We rewrite Eq. (6.31) with account of the fact that $dW = p\,dV$. We get

$$dS = \frac{dU + p\,dV}{T}$$

or

$$dU = T\,dS - p\,dV \tag{6.34}$$

Any two of the four quantities $T$, $S$, $p$, and $V$ in this equation can be chosen as independent variables through which the remaining ones will be expressed.

It is known from the course in mathematical analysis that if $x$ and $y$ are independent variables of the function $U(x, y)$ and $dU$ is its total differential, then

$$dU = \frac{\partial U}{\partial x}\,dx + \frac{\partial U}{\partial y}\,dy \quad \text{and} \quad \frac{\partial^2 U}{\partial x\,\partial y} = \frac{\partial^2 U}{\partial y\,\partial x}$$

Double differentiation of Eq. (6.34) yields

$$\frac{\partial T}{\partial x}\frac{\partial S}{\partial y}-\frac{\partial T}{\partial y}\frac{\partial S}{\partial x}=\frac{\partial p}{\partial x}\frac{\partial V}{\partial y}-\frac{\partial p}{\partial y}\frac{\partial V}{\partial x} \tag{6.35}$$

We can substitute any two of the four quantities $T$, $S$, $p$, and $V$ for $x$ and $y$ in this equation. Suppose, for instance, that the state of the system changes owing to a change in the volume by $dV$ and the temperature by $dT$. Let us calculate the resulting change in the entropy $dS$.

This means that in Eq. (6.35) we must substitute $V$ for $x$ and $T$ for $y$, i.e.

$$\frac{\partial T}{\partial V}\frac{\partial S}{\partial T}-\frac{\partial T}{\partial T}\frac{\partial S}{\partial V}=\frac{\partial p}{\partial V}\frac{\partial V}{\partial T}-\frac{\partial p}{\partial T}\frac{\partial V}{\partial V}$$

but if $T$ and $V$ are independent variables, then $\partial T/\partial V=\partial V/\partial T=0$ and, consequently, we have

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V \tag{6.36}$$

In addition, let us take into account that $dS$ is a total differential:

$$dS=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV \tag{6.37}$$

The last equation signifies that the total increase in the entropy consists of its increases due separately to the increase in temperature and in volume. It follows from Eqs. (6.36) and (6.37) that

$$dS=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial p}{\partial T}\right)_V dV \tag{6.38}$$

The first term in the right-hand side of Eq. (6.38) is the change in the entropy $(dS)_V$ due only to the change in temperature at constant volume ($dV=0$). According to the definition [see Eq. (6.30)], we have

$$(dS)_V=\frac{(dQ)_V}{T}$$

where $(dQ)_V$ is the quantity of heat supplied to a body for changing its state at constant volume, i.e.

$$(dQ)_V=C_V\,dT$$

here $C_V$ is the heat capacity of the body at constant volume; consequently,

$$\left(\frac{\partial S}{\partial T}\right)_V dT=\frac{C_V}{T}\,dT$$

and finally

$$dS = \frac{C_V}{T}\,dT + \left(\frac{\partial p}{\partial T}\right)_V dV \tag{6.39}$$

We have thus expressed $dS$ through the experimentally measured quantities $p$, $V$, $T$, and $C_V$.

In exactly the same way, we can express the change in the entropy $dS$ through the change in the temperature $dT$ and in the pressure $dp$, i.e. choose $T$ and $p$ as the independent variables. For this purpose, we must use $T$ and $p$ in Eq. (6.35) instead of $x$ and $y$. We get

$$\frac{\partial T}{\partial T}\frac{\partial S}{\partial p} - \frac{\partial T}{\partial p}\frac{\partial S}{\partial T} = \frac{\partial p}{\partial T}\frac{\partial V}{\partial p} - \frac{\partial p}{\partial p}\frac{\partial V}{\partial T}$$

But $\partial T/\partial p = \partial p/\partial T = 0$ because $T$ and $p$ are independent variables. As a result, we get an equation similar to Eq. (6.36):

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{6.40}$$

and correspondingly by analogy with Eq. (6.39)

$$dS = \frac{C_p}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_p dp \tag{6.41}$$

By integrating Eqs. (6.39) and (6.41), we can calculate the entropy $S(V, T)$ of a given mass (for instance one mole) of a substance at given values of the volume $V$ and the temperature $T$, or the entropy $S(p, T)$ at given values of the pressure $p$ and the temperature $T$ if we know the values of the entropy $S(V_0, T_0)$ and $S(p_0, T_0)$ at some other values of the parameters $V_0$ and $T_0$ or $p_0$ and $T_0$. It is obvious that

$$S(V, T) - S(V_0, T_0) = \int_{T_0, V_0}^{T, V_0} \frac{C_V\,dT}{T} + \int_{T, V_0}^{T, V} \left(\frac{\partial p}{\partial T}\right)_V dV$$

and

$$S(p, T) - S(p_0, T_0) = \int_{p_0, T_0}^{p_0, T} \frac{C_p\,dT}{T} - \int_{p_0, T}^{p, T} \left(\frac{\partial V}{\partial T}\right)_p dp$$

Particularly, for one mole of an ideal gas, we have

$$\int_{T_0}^{T} \frac{C_V\,dT}{T} = C_V \ln \frac{T}{T_0}$$

$$\int_{V_0}^{V} \left(\frac{\partial p}{\partial T}\right)_V dV = R \ln \frac{V}{V_0} \text{ because } \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

and we get

$$\Delta S = S(V, T) - S(V_0, T_0) = C_V \ln \frac{T}{T_0} + R \ln \frac{V}{V_0} \tag{6.42}$$

Equation (6.42) shows, particularly, that the entropy grows both with an increase in the volume of a gas and with an increase in its temperature. Thus, if an ideal gas expands isothermally, i.e. $T = T_0$, the change in the entropy is

$$\Delta S = R \ln \frac{V}{V_0} \tag{6.43}$$

**Dependence of Internal Energy on Volume.** We have already drawn the reader's attention (see Sec. 5.13) to the fact that in real gases the internal energy $U$ depends not only on the temperature $T$, but also on the volume $V$ (density) of a gas:

$$U = f(T, V)$$

It was indicated in the same section that the change in the internal energy due to a change in the volume at constant temperature is determined by Eq. (5.26), namely,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Now, using the obtained thermodynamic relationships, we can derive this important equation. For this purpose, let us again use the thermodynamic identity (6.31) in the form

$$dS \equiv \frac{dU + p\,dV}{T} \equiv \frac{1}{T} dU + \frac{1}{T} p\,dV$$

It follows from $dU$ being a total differential that

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

i.e. the total change in the internal energy of a system is composed of the changes due separately to the change in the volume $(\partial U/\partial V)_T\,dV$ and the change in the temperature $(\partial U/\partial T)_V\,dT$. Hence, it follows in turn that

$$dS = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV + \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT \tag{6.44}$$

Let us compare with Eq. (6.44) the equation (6.38) obtained above:

$$dS = \left(\frac{\partial p}{\partial T}\right)_V dV + \left(\frac{\partial S}{\partial T}\right)_V dT \tag{6.45}$$

A comparison of the coefficients of $dV$ in Eqs. (6.44) and (6.45) shows that

$$\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] = \left(\frac{\partial p}{\partial T}\right)_V$$

whence we obtain the expression we are interested in:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{6.46}$$

It is useful to note that the term $T(\partial p/\partial T)_V$ is nothing but $dQ/dV$, i.e. the quantity of heat per unit change of volume which must be imparted to a body for its volume to grow with the temperature remaining constant.

For an ideal gas,

$$T\left(\frac{\partial p}{\partial T}\right)_V = p \quad \text{and therefore} \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Let us use Eq. (6.46) for calculating the internal energy of a gas whose state is described by the van der Waals equation

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

It can easily be seen that here

$$T\left(\frac{\partial p}{\partial T}\right)_V = \frac{RT}{V-b} \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

Hence,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V\, dT + \frac{a}{V^2} dV$$

and, therefore,

$$U = \int C_V\, dT + \int \frac{a}{V^2} dV = C_V T - \frac{a}{V} + B$$

where $B$ is an integration constant. Its value can be determined from the condition that at $V \to \infty$, i.e. when a gas becomes infinitely rarefied, it must have the properties of an *ideal* gas for which

$$U = C_V T = \frac{i}{2} RT$$

(here $i$ is the number of degrees of freedom of a gas molecule). But this means that $B = 0$, and the internal energy of a van der Waals gas is

$$U = C_V T - \frac{a}{V} \tag{6.47}$$

Hence it follows that the internal energy of such a gas is composed of the kinetic energy of the molecules ($C_V T$) which is determined by the temperature and the potential energy ($-a/V$) due to the forces of interaction of the molecules. It is clear that the potential energy diminishes in its numerical value with an increase in the distance between molecules (because the forces of interaction diminish here), i.e. with an increase in the volume occupied by the gas.

## 6.14. ENTROPY IN REVERSIBLE PROCESSES IN A CLOSED SYSTEM

If an adiabatic process occurs in a system, this means that the latter is closed. It is closed in the sense that it is isolated from external sources of heat, both those giving up heat to it and those absorbing heat. If the process of the change in state in such a system is reversible, then the change in the entropy equals zero because the quantity $dQ$ in the equation

$$dS = \frac{dQ}{T}$$

equals zero. *The entropy of a closed system remains unchanged upon an adiabatic change in its state.*

True, bodies that are external with respect to such a system may perform work on it, and the system itself may perform work on external bodies. In this sense, the system is not closed. But if we include these bodies in our system, the change in the entropy in such an already completely closed system remains equal to zero as before because the changes in the state of bodies doing work or of bodies on which work is being done are not attended by changes in the entropy — these are purely mechanical parts of our system.

But we can show that the entropy does not change upon *any reversible change* in the state of a closed system.

Indeed, suppose that a certain body capable of expanding or being compressed exchanges heat with heat sources — it receives heat from one group of the sources or transfers heat to the others. Suppose also that work is done on the body or the body itself does work. Let us call the bodies that do work or on which work is done sources of work. We shall consider a closed system including the body itself, the sources of heat, and the sources of work.

Assume that the state of the body changes *reversibly* because of its exchanging heat with the heat sources and of its doing work or work being

done on it. The performance of work (of any sign), as we have just seen, does not lead to a change in the entropy. The latter changes only when heat is exchanged between a body and heat sources. If a body, for example, received the heat $dT_{body}$ from a source, its entropy changed by the amount $dQ_{body}/T$, where $T$ is the temperature of the body. But the source lost the same quantity of heat. If we denote the quantity of heat lost by $dQ_{source}$, it is quite evident that $dQ_{body} = -dQ_{source}$. The entropy of the heat source will change by the amount $-dQ_{source}/T$, where $T$ is the temperature of the source. Since the process of heat exchange is reversible, the temperature of the body should equal that of the source. Otherwise, an irreversible process of thermal conductivity will take place. It is therefore clear that

$$\frac{dQ_{body}}{T} = -\frac{dQ_{source}}{T} \quad \text{or} \quad dS_{body} = -dS_{source}$$

The total change $dS$ in the entropy of the entire closed system equals zero:

$$dS = dS_{body} + dS_{source} = 0$$

Consequently, *the entropy of a closed system remains unchanged when any reversible process occurs in it.*

## 6.15. ENTROPY IN IRREVERSIBLE PROCESSES IN A CLOSED SYSTEM. LAW OF INCREASE IN ENTROPY

An important feature of entropy is its behaviour in irreversible processes. We saw in Sec. 6.12 that the relationship

$$\oint \frac{dQ}{T} < 0$$

holds for an irreversible cyclic process. It is a generalization of the particular expression

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0$$

which, in turn, is a corollary of Carnot's first theorem.

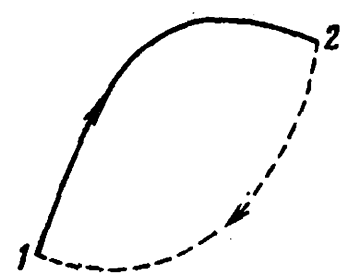


Fig. 95

Let us consider a process in which a system irreversibly passes from equilibrium state *1* to equilibrium state *2* (it is shown by a solid line in Fig. 95). Irreversibility of the transition signifies that the intermediate states are not equilibrium ones. How will the entropy of the system change in such a transition? To find this out, let us return the system to its initial state along a *reversible* path, for instance along the one

depicted by the dash line in Fig. 95. The cyclic process obtained is irreversible because one of its parts is irreversible. Hence, the expression

$$\oint \frac{dQ}{T} < 0$$

holds for it. But

$$\oint \frac{dQ}{T} = \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ}{T}$$

The second of the two integrals, since it relates to a reversible process, equals

$$\int_2^1 \frac{dQ}{T} = S_1 - S_2$$

Consequently,

$$\int_1^2 \frac{dQ}{T} + S_1 - S_2 < 0 \quad \text{or} \quad S_2 - S_1 > \int_1^2 \frac{dQ}{T}$$

If the system is closed, i.e. isolated from heat sources, then $dQ = 0$, and

$$S_2 - S_1 > 0 \quad \text{or} \quad S_2 > S_1$$

The conclusion is that *the entropy of a closed (i.e. adiabatically isolated) system grows in an irreversible process.*

Bearing in mind what we found out in the preceding section, we can say that the entropy of a closed system either remains constant or grows.

The law of the growth in the entropy in irreversible processes is one of the very significant features of the value of the entropy. It is moreover important because, as we have already noted, the concept of a reversible process is an idealization. We know that in a reversible process a system at any stage of the process must be in a state of thermodynamic equilibrium. Time is needed for equilibrium to set in, and, therefore, for a process to be fully reversible it must proceed infinitely slowly which, naturally, never happens.

Experiments and theory show, however, that for irreversible processes in closed systems the entropy always grows, and this property is inherent in entropy just like the total energy has the property of remaining constant in any processes in closed systems.

It is exactly because the energy has the property of remaining constant in a closed system that it cannot serve as a function showing the direction

in which processes occur in such a system. Upon any change in state, the energy at the beginning and the end of a process is the same, and it therefore does not permit the initial and final states to be distinguished from each other. The entropy, on the contrary, which always grows in naturally occurring processes, makes it possible to see what direction of a process is possible and what is not, what state is the initial one and what is the final one.

If, for example, we mix masses of water having different temperatures, it is easy to see that the sum of the entropies of the two masses before mixing is less than the entropy of the mixture which has an intermediate temperature. It is clear that the mixing process can proceed by itself, but the reverse process of separating the mixed masses cannot proceed in any way because it would be attended by a decrease in the entropy.

The increase in the entropy in any process continues not unlimitedly, but only to a definite maximum value characteristic of the given system. This maximum value of the entropy corresponds to the state of *equilibrium*, and after it has been reached all changes that do not involve external action stop.

Thus, the entropy as a function of state appreciably differs from the energy. Whereas energy can neither be created nor destroyed, entropy can be created, and it is constantly created in any process of transition to equilibrium. But once created, it can no longer be destroyed: the reverse process with diminishing of the entropy cannot occur.

The law of the *increase in entropy* in irreversible processes is also often called the *second law of thermodynamics*.

We shall give a few examples illustrating this law.

**Increase in the Entropy in Heat Transfer.** If we bring into contact two bodies $A$ and $B$ whose temperatures equal $T_A$ and $T_B$, then heat will transfer from the hotter body to the colder one, and as a result the temperatures of the two bodies will level out.

Assume that $T_A > T_B$. Let us calculate the change in entropy that attends this irreversible process.

The state of body $A$ changes as a result of its *losing* a certain quantity of heat $-dQ$. Body $B$ changes its state accordingly as a result of *receiving* the same quantity of heat $+dQ$.

To determine the change in the entropy of the system formed of the two bodies, we must calculate the value of $dQ/T = dS$ for a *reversible* process leading to the same change in the state of the system (see p. 272). We can use as such a process, for example, the transfer of heat from body $A$ to body $B$ with the aid of a third *working* body as was done in considering the Carnot process which is conducted reversibly in all its stages. Hence for body $A$ and correspondingly for body $B$, we have

$$dS_A = -\frac{dQ}{T_A} \quad \text{and} \quad dS_B = \frac{dQ}{T_B}$$

The total change in the entropy of both bodies is

$$dS = \left( \frac{1}{T_B} - \frac{1}{T_A} \right) dQ \tag{6.48}$$

Since $T_A > T_B$, then $dS > 0$, i.e. *the entropy of the system grows.*

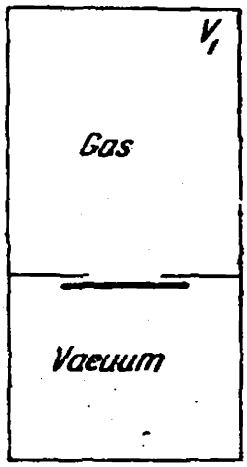


Fig. 96

The above reasoning does not depend on the process used to transfer heat from body $A$ to body $B$ — thermal conductivity or radiation. It is only important that the temperatures of the two bodies be different.

**Growth of Entropy in Adiabatic Expansion of an Ideal Gas into a Vacuum.** We have already noted that the expansion of a gas into a vacuum is an irreversible process. We shall now show that the process is attended by a growth of the entropy.

Imagine a vessel with thermal-insulating walls separated into two parts by a partition with an opening closed by a register or shutter (Fig. 96). Let one part of the vessel having the volume $V_1$ be filled with one mole of an ideal gas whereas the other part is free of the gas. If we open the shutter, the gas will expand adiabatically and fill the entire volume $V$ of the vessel. We know that the temperature of the gas will not change during the expansion (Joule's experiment, see Sec. 2.14).

At first sight, it seems that the entropy of the gas should not change upon such expansion because no heat is taken away from it or supplied to it. Matters are different, however. The process of expansion in the above experiment is irreversible, and the relationship $dS = dQ/T$ cannot be applied to it. In an irreversible process the quantity $dQ/T$ is not a differential of a function of state. Particularly, the integral $\int \frac{dQ}{T}$ does not equal the change in the entropy.

Actually, the entropy of the gas upon adiabatic expansion into a vacuum changes. To find this change, we must calculate the change in the entropy in a reversible process resulting in the same change in state. The reversible isothermal expansion of the gas at the same temperature may be such a process, for example. In Sec. 6.13, we have already performed such a calculation. It showed us that in the isothermal reversible expansion of one mole of a gas into a vacuum the change in the entropy $\Delta S$ equals [see Eq. (6.43)]

$$\Delta S = R \ln \frac{V}{V_1} \tag{6.49}$$

Since $V > V_1$, then $\Delta S > 0$, i.e. the entropy grows when a gas expands.

***Growth of Entropy in the Interdiffusion of Gases.*** If we bring two different gases into contact, they will mix owing to interdiffusion by themselves,

without any external action. The reverse process, i.e. the separation of a gas mixture into its components, does not occur by itself and is possible only when there is a definite external action. The mixing of gases is an irreversible process. It should therefore be attended by a growth of the entropy.

Indeed, imagine that a vessel having the volume $V_1$ contains one mole of an ideal gas. Another vessel having the volume $V_2$ contains one mole of another gas. Let us connect the two vessels. The gases mix when this is done, and the mixture formed occupies the volume $V = V_1 + V_2$. This process can be considered as expansion of each of the gases: the first one expands from the volume $V_1$ to the volume $V$, and the second from $V_2$ to $V$. The entropy of the first gas, as we have just seen, changes by the quantity $R \ln (V/V_1)$, and of the second gas by $R \ln (V/V_2)$. The total change in the entropy $\Delta S$ will be expressed by the equation

$$\Delta S = R\left(\ln \frac{V}{V_1} + \ln \frac{V}{V_2}\right) \tag{6.50}$$

Since both $V_1$ and $V_2$ are less than $V$, then $\Delta S > 0$, i.e. the entropy of the system has increased.

## 6.16. THE SECOND LAW OF THERMODYNAMICS AND THE CONVERSION OF HEAT INTO WORK

When mechanical energy transforms into heat, the process goes on very simply: all of the mechanical energy entirely transforms into heat, and to find out how many calories will be obtained in such a conversion it is sufficient to multiply the number of joules of work done by 0.239 (the heat equivalent of mechanical work). The efficiency will therefore always equal unity.

We have already seen in Sec. 6.8 that the reverse process of obtaining mechanical work at the expense of heat is much more complicated.

We said about the heat engine operating according to the Carnot cycle and described in Sec. 6.8 that it is the best of all conceivable heat engines, and that no other engine in the same temperature conditions can give a greater quantity of work. The efficiency of this best engine, however, is always less than unity, and it is often surprisingly small. If, for instance, the temperature $T_0$ of the heat source is 373 K (the boiling point of water) and of the heat sink $T_1 = 293$ K (room temperature), then the efficiency of an ideal Carnot machine found by Eq. (6.18), i.e. $\eta = 1 - (T_1/T_0) = 1 - (293/373) = 0.21$ or only 21%. And this efficiency is the upper (and unattainable) limit! In real machines such as those used on steam locomotives in their time, the efficiency rarely exceeds 10%.

Thus, the possibilities of the continuous (cyclic) obtaining of work at the expense of heat are restricted in a definite way in the sense that the heat taken away from the source cannot be completely converted into work. The possibility of obtaining work at the expense of heat, generally speaking,

has a high price in the form of the uselessly lost heat given up to the heat sink.

It is easy to see that it is exactly the second law of thermodynamics which imposes these restrictions.

Suppose we have a vessel with an ideal gas. Let us first assume that the second law of thermodynamics is not valid. This means that the molecules of the gas may occupy the entire volume of the vessel, but may also gather in any small part of it (neither the laws of mechanics nor the first law of thermodynamics prevent this).

After catching the moment when the gas gathers by itself in a part of the volume of the vessel and is thus compressed, we can separate it from the remaining part of the vessel by means of a damper in the form of a piston. Next, letting the gas expand, we can make it perform the work of moving the piston. To prevent cooling of the gas during expansion, we shall ensure its thermal contact with the surroundings from which it will draw heat (the expansion is therefore isothermal).

After the gas has done work the first time, we can wait until it gathers again in a part of the vessel (if, as we assumed, the second law of thermodynamics is not valid, our waiting should not be in vain), and once more permit it to expand and do work. Such cycles can be repeated an endless number of times.

Hence, we can use this principle to construct a machine operating in cycles whose action will have as its only result the performance of work and cooling of a heat source, i.e. in essence it will be a "perpetual motion machine". But this machine does not contradict the law of conservation of energy. We can see that here work is done not "from nothing", but at the expense of the heat which the gas takes from the surroundings. Since we can consider that the stores of energy in the atmosphere, in the water of the seas and oceans, and in the Earth's crust are inexhaustible, such a machine would virtually not differ from a perpetual motion machine.

The above hypothetic heat machine or engine whose operation consists only in performing mechanical work at the expense of heat is called a *perpetual motion machine of the second kind,* in contrast to a *perpetual motion machine of the first kind* in which, in violation of the law of conservation of energy, more work is created than energy is spent. The efficiency of this machine would equal unity because in an isothermal process of expansion of an ideal gas we have $dW = dQ$.

Actually, however, such a machine cannot function because we shall wait in vain for the molecules of the gas to gather by themselves in a part of the volume of the vessel. Such spontaneous concentration of molecules would be attended by a decrease in the entropy and is therefore impossible. It should be noted that here we are dealing with the impossibility of a *cyclic* machine that constantly repeats the process of converting heat into work. This is very important because a single conversion of this kind is

quite possible — it contradicts neither the first nor the second law of thermodynamics.

The second law of thermodynamics is sometimes even expressed in the form of a statement that a perpetual motion machine of the second kind is impossible, just like the first law can be expressed in the form of the statement that a perpetual motion machine of the first kind is impossible.

The second law of thermodynamics also answers the question as to what is needed for a cyclic machine *to be able* to function.

We cannot simply take heat away from a heat source with the aid of a working body and convert this heat into work because such a process is accompanied by a reduction of the entropy of the source (the working body performs a cyclic process and its entropy remains unchanged). Hence, we must have a system consisting not of two bodies — a heat source and a working body, but of three, and the part played by the third body must consist in that its entropy should grow by at least the same amount by which the entropy of the heat source diminishes as a result of heat being taken away from it ($dS = dQ/T$). For the entropy of the third body to grow, it must be given part of the heat taken from the heat source. The heat sink is this third body. Since its temperature is lower, then less heat needs to be transferred to it than is taken away from the heat source so that part of this heat can be converted into work. In these conditions, the entropy of the system "heat source-working body-heat sink" remains constant. This is already permitted by the second law of thermodynamics which forbids only processes with a reduction of the entropy.

Hence it follows that in principle we cannot use a cyclically functioning machine to convert into work all the heat received by the working body from the heat source. We must transfer part of it without fail to the heat sink. This is the price which we have to pay for transforming the other part of the heat into work.

Above we considered the case when such an amount of heat is transferred to the heat sink that increases its entropy exactly by the quantity needed to compensate for the reduction of the entropy of the heat source. This is clearly the minimum amount of heat lost without which a machine in general cannot function. The entropy remains constant, and the maximum fraction of the heat received from the source is converted into work. Hence, the efficiency of the machine will be maximum. We already know that constancy of the entropy corresponds to a reversible process. This is why an ideal machine having the maximum efficiency must be reversible. It is exactly for this reason that when describing the Carnot cycle we attracted attention to the fact that in this cycle no irreversible thermal conductivity processes occur, but expansion and compression proceed reversibly.

In a real machine, we cannot ensure completely reversible processes in all the stages of a cycle. Therefore, the entropy will grow instead of remaining constant. This, in turn, means that in a real machine more heat will

have to be transferred to the heat sink than that determined by the equation $Q_0/T_0 = Q_1/T_1$.

Consequently, a greater part of the heat received from the heat source than in a reversible machine will become unavailable for the conversion into work in this case, and the efficiency of the machine will be less than that calculated for the reversible Carnot cycle.

An increase in the entropy in general means that heat becomes *less available for its conversion into mechanical work*. This can easily be seen from the following calculations.

Imagine a heat source with the temperature $T_1$ that transmits the quantity of heat $Q$ to the working body. If the temperature of the heat sink is $T_0$, then the quantity of heat $Q_0$ transferred to it is determined from the equation $Q/T_1 = Q_0/T_0$, whence

$$Q_0 = Q\frac{T_0}{T_1}$$

The quantity of heat that can be converted into work is

$$Q - Q_0 = Q\left(1 - \frac{T_0}{T_1}\right)$$

If we take a different heat source having the temperature $T_2$ and take away the same quantity of heat $Q$ from it, we shall have to transfer the quantity of heat $Q_0'$ to the heat sink (having the previous temperature $T_0$). This quantity is determined from the equation $Q/T_2 = Q_0'/T_0$, whence

$$Q_0' = Q\frac{T_0}{T_2}$$

and a quantity of heat equal to

$$Q - Q_0' = Q\left(1 - \frac{T_0}{T_2}\right)$$

can be converted into work in this case.

Hence it follows that if the quantity of heat $Q$ transfers from the body with the temperature $T_1$ to one with the temperature $T_2$, the "working ability" of the heat (i.e. the magnitude of the part of it that can be converted into work) changes by the amount

$$Q\left(1 - \frac{T_0}{T_2}\right) - Q\left(1 - \frac{T_0}{T_1}\right) = Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right)T_0 \qquad (6.51)$$

According to Eq. (6.48), the expression $Q(1/T_1 - 1/T_2)$ equals the *increase* in the entropy, taken with the reverse sign, when heat passes from a body having the temperature $T_1$ to one having the temperature $T_2$ (where $T_1 > T_2$). Consequently, the change in the "working ability" of heat when

it passes from one body to another is determined by the *change in the entropy* in such a transfer. Inspection of Eq. (6.51) shows that a *growth* of the entropy results in a *decrease* of the availability of heat for conversion into work. Growth of the entropy leads, as it were, to the devaluation of heat energy, to diminishing of the possibility of obtaining work at its expense. From this viewpoint, the second law of thermodynamics can be considered as a statement that in any closed system a process (irreversible!) goes on so that the quantity of energy capable of being converted into work diminishes and tends to zero in equilibrium.

It is therefore clear that the free energy which we introduced on an earlier page and which is the part of the energy that in an isothermal process ($dT = 0$) can be converted into mechanical work is related to the entropy.

Let us write an equation of the law of conservation of energy:

$$dQ = dU + dW$$

Since $dS = dQ/T$, then $dQ = T\,dS$, and our equation becomes

$$dU = T\,dS - dW \tag{6.52}$$

It follows from Eq. (6.52) that

$$-dW = dU - T\,dS = d(U - TS)$$

or

$$dW = -d(U - TS) \tag{6.53}$$

($S\,dT = 0$ because $T = \text{const}$).

Equation (6.53) shows that the work $dW$ in an isothermal process equals the change in a certain function $U - TS$ (see p. 267). The latter is obviously the free energy $A$ of the system:

$$A = U - TS \tag{6.54}$$

(This is the formula we promised the reader on p. 268.)

The free energy, i.e. the energy capable of producing mechanical work, therefore equals the internal energy $U$ minus the quantity $TS$. It is clear that $TS$ is the part of the energy that cannot be converted into work, and it is the greater, the greater is the entropy. The quantity $TS$ is therefore sometimes called the *bound energy*.

The quantity in the right-hand side of Eq. (6.51) is exactly the *change* in the bound energy $T_0 \Delta S$. It equals the *change* in the "working ability" of heat energy.

## 6.17. PHYSICAL MEANING OF ENTROPY. ENTROPY AND PROBABILITY

The second law of thermodynamics states that irreversible processes (and these include virtually all heat processes and at any rate all naturally occurring processes) proceed so that the entropy of the system of bodies

participating in a process grows, tending to a maximum value. The maximum value of the entropy is reached when the system arrives at a state of equilibrium.

At the same time, we have seen in Sec. 6.4 that the irreversibility of heat processes itself is connected with the fact that the transition to the equilibrium state is overwhelmingly more probable in comparison with all other transitions. This is why we only observe such changes of state in which a system passes from a less probable to a more probable state. The similarity in the behaviour of the two quantities — entropy and probability — is striking: both of them grow upon a transition to equilibrium. It is therefore natural to relate the entropy of a system in a certain state to the probability of this state. *This relationship was discovered by L. Boltzmann.*

First of all we must define more precisely the concept of the probability of a state. This can be done in the simplest way if we again, as in Sec. 6.4, use the example of the distribution of gas molecules in the volume of a vessel.

Imagine a vessel divided into two parts, and let it contain, for example, six molecules each of which will be mentally given a definite number to enable us to "distinguish" them from one another. It is easy to see by simple calculations that these six molecules can be arranged in the two halves of the vessel in 64 different ways. A definite state of the system corresponds to each of them. For instance, the state in which the left-hand part of the vessel contains one molecule and the right-hand part five differs from the state when these two parts contain two and four molecules, respectively. Let us see in how many ways of the total number of possible arrangements of the molecules each state of our system can be realized. It is not difficult to calculate that, for example, only one arrangement (combination) creates a state when the left-hand part of the vessel does not contain a single molecule. The state "one in the left-hand, five in the right-hand part" can be accomplished in six ways, and the state "two in the left-hand, four in the right-hand part" in 15 ways. The greatest number of combinations results in a state when there will be three molecules in each of the two parts, i.e. the molecules will be uniformly distributed between the two halves of the vessel.

We can show in general that if a vessel contains $N$ molecules and they are numbered, then they can be distributed in $2^N$ ways between the two halves of the vessel. Among this total number of different combinations, the number $C$ of combinations when one half of the vessel (for instance the left-hand one) contains $n$ molecules and the other half $N - n$ molecules is determined by the equation

$$C = \frac{N!}{n!(N-n)!}$$

(here the number 0! is considered equal to 1). It is simple to convince ourselves that at any value of $N$ the value of $C$ will be the greatest when $n = N/2$, i.e. uniform distribution of the molecules throughout the volume of the vessel is accomplished in the greatest number of ways.

The same result will be obtained if we divide our vessel not into two, but into an arbitrary number of parts.

It is easy to pass over to the probability of a certain distribution of the particles between the two halves of a vessel. If in the example considered above with six molecules the total number of combinations of the molecules is 64, and six of them result in a state when the left-hand part of the vessel contains one molecule, then the probability of this state is obviously 6/64. The probability of uniform distribution is 20/64. In general, the probability $P$ of the left-hand part of the vessel containing $n$ of the $N$ particles is

$$P = \frac{N!}{n!(N-n)!\,2^N} \tag{6.55}$$

It is clear that the probability $P$ also has a maximum at $n = N/2$.

When the number of molecules $N$ is very great, the number of ways in which the molecules are distributed uniformly in the volume of the vessel becomes overwhelmingly great in comparison with any other non-uniform distribution. In the course of the continuous chaotic thermal movements of its molecules, a gas may be in any of the conceivable states, but in the predominating majority of cases we shall naturally find it in a state corresponding to the maximum number of combinations, i.e. in a state of uniform distribution. It is this state that is the equilibrium one. And if a gas is not in equilibrium for some reason or other, it will inevitably pass over to this state when left alone.

Thus, every state of a system can be characterized not only by its mathematical probability $P$ determined by Eq. (6.1), i.e.

$$P = \left(\frac{V'}{V}\right)^N$$

but also by the number of ways in which this state can be achieved. The latter quantity is called the *thermodynamic probability* and is designated by the symbol $W$.

It is clear that both these probabilities are related to each other. But unlike $P$, which is always less than unity, the thermodynamic probability $W$ is expressed by great numbers.

The entropy can be related to the value of the thermodynamic probability because both these quantities have a maximum value in the state of equilibrium, and the transition of any system to equilibrium is attended by a growth of both the entropy and the thermodynamic probability.

For reasons which we shall not stop to consider here, Boltzmann related the entropy $S$ and the thermodynamic probability $W$ by the expression

$$S = k \ln \frac{W}{W_0} \tag{6.56}$$

where $k$ is the Boltzmann constant, as previously.

Equation (6.56) can also be written as follows:

$$S = k \ln W - k \ln W_0 = k \ln W - S_0$$

The quantity $S_0 = k \ln W_0$ can be taken as the zero from which the entropy is counted. Hence, the entropy counted from this zero will be expressed by the equation

$$S = k \ln W \tag{6.57}$$

Sometimes, the thermodynamic probability of a system being in a given state is determined in a different way whose idea can be explained by the following example.

In Sec. 6.4, we saw that the probability of a state in which a gas consisting of $N$ molecules is concentrated in a part of the volume of a vessel $V'$ equal to $V/m$ is

$$P = \left(\frac{1}{m}\right)^N = \frac{1}{\left(\frac{V}{V'}\right)^N} = \left(\frac{V'}{V}\right)^N$$

Let us introduce the reciprocal of this quantity

$$W = \frac{1}{P} = \left(\frac{V}{V'}\right)^N \tag{6.58}$$

It shows how many times the probability $P$ is less than the probability of the fact that the gas will occupy the entire volume of the vessel (this probability equals unity because $V'$ is part of the volume $V$).

If the values of the mathematical probability $P$ of the state of a molecular system (at great values of $N$) are always very small, then the values of the thermodynamic probability $W$, on the contrary, are very great. The minimum value of $W$ in our example equals unity (when $V' = V$) whereas for $P$ unity is its maximum value (also when $V' = V$).

It is the quantity $W$ determined by Eq. (6.58) that is called the thermodynamic probability. It is obvious that both definitions of the thermodynamic probability given above do not contradict each other.

Let us write Eq. (6.58) for one mole of a substance:

$$W = \left(\frac{V}{V'}\right)^{N_A}$$

where $N_A$ is the Avogadro constant. Since $N_A = R/k$, then

$$W = \left(\frac{V}{V'}\right)^{R/k}$$

Taking logarithms of this equation, we get

$$\ln W = \frac{R}{k} \ln \frac{V}{V'}$$

or

$$k \ln W = R \ln \frac{V}{V'} \tag{6.59}$$

According to Boltzmann's equation (6.57), i.e. $S = k \ln W$, the quantity in the left-hand side of Eq. (6.59) is the entropy.

Assume that a mole of a gas expands isothermally from the volume $V' = V_1$ to the volume $V' = V_2$. Using Eq. (6.59), let us write expressions for the entropy of the gas before and after expansion:

$$S_1 = k \ln W_1 = R(\ln V - \ln V_1)$$

$$S_2 = k \ln W_2 = R(\ln V - \ln V_2)$$

Subtracting one expression from the other, we get the value of the change in the entropy as a result of expansion:

$$|\Delta S| = |S_2 - S_1| = k \ln \frac{W_1}{W_2} = R \ln \frac{V_2}{V_1} \qquad (6.60)$$

We have obtained a similar formula on an earlier page [see Eq. (6.43)].

The work of expansion in an isothermal process is

$$W_{ex} = RT \ln \frac{V_2}{V_1}$$

Comparing this equation with Eq. (6.60), we get

$$\Delta S = \frac{W_{ex}}{T}$$

On the other hand, according to the law of conservation of energy, in an isothermal process $W_{ex} = \Delta Q$, whence

$$\Delta S = \frac{\Delta Q}{T}$$

We have thus obtained the same expression for $\Delta S$ as we did earlier from our analysis of the Carnot cycle.

The relationship between the entropy and probability permits us to interpret the second law of thermodynamics in a somewhat different way. Now it means that any process in nature proceeds so that a system passes over into a state whose probability is greater. At the same time, the statement contained in the second law loses its categorical nature. The circumstance that any spontaneously occurring process results in a state having a greater probability does not mean that another direction of the process is impossible. We have already indicated that it only points to the transition to equilibrium being just more probable than spontaneous departure from the equilibrium state. Therefore, the second law actually has to be understood as follows: if a system is in a state with a given entropy, it should be expected with an overwhelming probability to pass over to a state with a greater entropy, i.e. *a growth of the entropy is its most probable change*. Processes attended by a decrease in the entropy are also conceivable in principle.

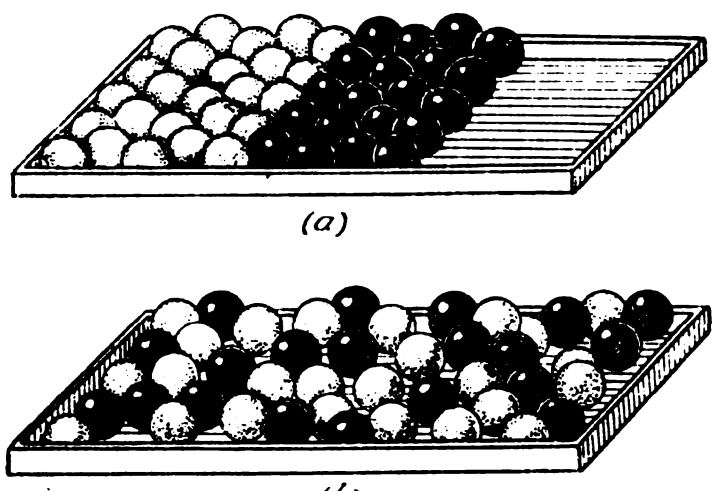
It should be remembered here that the fluctuations which we mentioned more than once are such changes of state that are attended by a decrease in the entropy (and, of course, of the probability). But these slight deviations from the equilibrium state do not contradict the second law. They are an inevitable corollary of the probabilistic nature of the entropy.

## 6.18. ENTROPY AND DISORDER

The heat energy of a body is the energy of the chaotic, disordered motion of its molecules. This disorder is what distinguishes the thermal motion of molecules from the macroscopic mechanical motion of a body when its constituent molecules move in an orderly manner. For instance in the translational motion of a body, all of its molecules travel at the same velocity which is superposed onto the velocities of their chaotic thermal motion. The conversion of heat energy into mechanical energy therefore consists in the transformation of chaotic thermal motion into ordered motion.

Conversely, to convert mechanical energy into heat energy means to convert the energy of order into that of disorder. It is not difficult to understand that these two opposite processes are not equivalent: it is incomparably simpler to convert ordered motion into chaotic motion than to perform the opposite transformation.

The following simple example will explain this. Imagine a case with black and white balls arranged so that the balls of each colour occupy a separate part of the case (Fig. 97*a*). It is now sufficient to shake the case a few times for the balls in it to move around and become arranged in complete disorder (Fig. 97*b*). Simple shaking converted order in the arrangement of the balls into disorder.



*(a)*

*(b)*

Fig. 97

We cannot, however, restore order in the case by shaking it so that the balls of the same colour would again occupy a separate part of it. Strictly speaking, if we repeat the shaking many times it is possible in principle

that order will be restored after one shaking of them. But such a chance event is obviously extremely improbable. Virtually every shaking results in disorder, and only one of a very great number results in order.

This distinctive irreversibility should manifest itself still more in a molecular system where the number of molecules is immeasurably greater than the number of balls in the case. Collisions between molecules "shake" the system and bring it into disorder even if order reigns in the system at a certain moment.

If two parts of a body are at different temperatures, then such a state of it is more ordered than the state in which its temperature has levelled out as a result of thermal conductivity. Similarly, if a vessel divided by a partition contains two different gases, this state of the system is more ordered than in a mixture of these gases, etc. Any natural process always goes on so that the system passes over to a state with greater disorder: the temperatures of bodies level out by themselves, gases mix by themselves, etc.

The similarity between the degree of disorder in a system and its entropy is obvious. It is therefore natural to consider the entropy as a measure of the disorder of a system. Having in view the relationship between the entropy and the probability of a state, we can say that a state with greater disorder is characterized by greater thermodynamic probability than a more ordered state.

The irreversibility of thermal processes also fits in here: they proceed so that the disorder in the system grows. The irreversibility of thermal processes is the irreversibility of order and disorder. Here also belongs the fact that any kind of energy transforms into heat in the long run because heat energy is energy of chaotic motion whereas all the other kinds of energy are connected with more ordered motion.

Summing up everything said above about entropy, let us formulate once more its main properties.

Entropy is a function of state of a system. To calculate the entropy of a system in a given state relative to a state taken as the zero one, we must calculate the value of $\int \frac{dQ}{T}$ in a *reversible* process that brings the system from the given state to the zero one. The entropy of the closed system remains constant if the system undergoes a *reversible* change of state. The entropy of a closed system that *irreversibly* changes its state grows. The maximum value of the entropy corresponds to equilibrium of the system. The entropy is directly connected with the probability of the state. The growth of the entropy of a system upon an irreversible change of its state means that the system passes over from a less probable to a more probable state. The entropy is a measure of the disorder of a system.

The growth of the entropy in an irreversible process means that the energy which a system has becomes less accessible for conversion into mechanical work. In a state of equilibrium, when the entropy has reached its maximum value, the energy of a system cannot at all be converted into work.

## 6.19. THE MAXWELL "DEMON"

J. Maxwell conceived the idea of the following mental experiment which at first sight contradicts the second law of thermodynamics.

Let us imagine a device that is capable of "feeling" separate molecules and place it in opening *O* of a wall that divides a vessel containing a gas into two parts (Fig. 98). Let the temperature and the pressure of the gas in both parts of the vessel be initially the same. Notwithstanding this circumstance, owing to their chaotic thermal movements, the molecules will continuously pass through the opening both from left to right and from right to left, the average number of molecules passing through the opening in either direction being the same so that the pressure and the temperature in both parts of the vessel do not change.

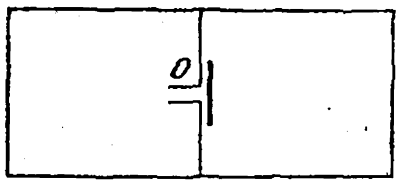


Fig. 98

Now let the device mentioned above, which Maxwell called a "demon", begin to function so that it lets only rapid molecules pass in one direction and only slow ones in the other. As a result after some time elapses, one half of the vessel — the one into which the demon let the rapid molecules pass — will contain molecules whose mean velocity is higher than those in the other half. This means that the gas in one half of the vessel will be at a higher temperature.

Thus, a difference in temperatures appears without any external work being done, which is a glaring contradiction of the second law of thermodynamics — the latter "permits" only levelling out of an existing temperature difference, but "prohibits" the spontaneous appearance of such a difference.

There is actually no contradiction here. The second law of thermodynamics can be applied only to macroscopic bodies containing a very great number of particles. This can be seen from the relationship existing between the entropy and probability. We cannot in general speak about this relationship if the number of particles is not great. For Maxwell's demon, however, a gas is not a macroscopic body since the demon is capable of selecting separate molecules, and the second law does not hold for them.

From the viewpoint of the mechanism of the phenomenon, Maxwell's paradox is solved as follows. Naturally giving up the idea of a demon situated at the opening with the intention of violating the second law of thermodynamics, we must have in mind a certain device. Since this device is brought into action by the impacts of molecules (let them even be only rapid ones), it itself should be of molecular dimensions. The components of this device will therefore participate in molecular thermal movements (such as Brownian motion). But these movements are quite chaotic and statistical ones. Hence, the opening will be opened according to the laws of chance so that not only rapid, but also slow molecules will be able to pass through it, and the expected temperature difference will not appear. This is in complete accordance with the second law of thermodynamics.

## 6.20. THE THERMODYNAMIC TEMPERATURE SCALE

In Chap. 1 when considering different ways of measuring temperature, we noted that a serious difficulty is encountered in such measurements. It consists in that the temperature scales established with the aid of various thermometric bodies do not coincide with one another.

We have just, however, acquainted ourselves with a property that does not depend at all on the kind of substance and can therefore serve as a faultless thermometric property for establishing a temperature scale. This property is that any substance when used as the working body in a reversible heat engine gives the same efficiency (naturally, at the same temperatures of the heat source and the heat sink).

If the working body, no matter what it is, absorbs the heat $Q_0$ at the temperature $T_0$ and gives up to the heat sink the heat $Q_1$ at the temperature $T_1$, then the following relationship holds:

$$\frac{Q_0}{T_0} = \frac{Q_1}{T_1} \quad \text{or} \quad \frac{Q_0}{Q_1} = \frac{T_0}{T_1} \tag{6.61}$$

The latter ratio, which holds for any substance, allows us to use the Carnot machine as a sort of thermometer. True, this "thermometer" makes it possible to determine only the ratio of two temperatures $T_0$ and $T_1$ and not the temperatures themselves. But if we agree to assign a definite numerical value to one of these temperatures or choose in some way or other the value of one degree of the change in the temperature interval, we shall thus determine the required temperature.*

We shall thus establish a temperature scale that does not depend on the kind of substance, i.e. a scale that is physically faultless.

Let us use an example to explain how the temperature is measured with such an unusual "thermometer". Suppose we have to measure the temperature $T$ of a body and have no thermometer at our disposal except for a Carnot machine.

We shall take as the heat source in the Carnot machine a heat reservoir at the boiling point of water (we shall naturally not measure this temperature because we have no thermometer for this purpose) and as the heat sink a heat reservoir at the temperature of melting ice (which we shall also not measure for the same reason). Let us also assume that we shall divide the difference between the temperatures of the heat source and the heat sink into 100 parts (degrees); we could choose any other number of parts and any other heat reservoirs. In addition to a Carnot machine, we need a calorimeter to measure the quantities of heat $Q_0$ and $Q_1$. In the Carnot

*By decision of the 10th General Conference on Weights and Measures (Conférence Générale des Poids et Mesures) in 1954, the temperature of the triple point of water (see Chap. 9) is the temperature which is given a definite numerical value. It is considered equal to 273.16 K.

"thermometer" the thermometric problem transforms into a calorimetric one!

Let us now conduct a reversible Carnot cycle between the heat source and the heat sink we have selected, using any working body (we know that nothing depends on it) and measure the quantity of heat $Q_{source}$ received from the heat source and $Q_{sink}$ given away to the heat sink. Let us denote by $T_{source}$, $T_{sink}$, and $T$ the temperatures (meanwhile unknown) of boiling water, melting ice, and the body being studied. Hence, we can write:

$$\frac{Q_{source}}{Q_{sink}} = \frac{T_{source}}{T_{sink}} \tag{6.62}$$

Next we conduct another Carnot cycle, but with the body being studied as the heat sink and with the previous heat source, or, conversely, with the previous heat sink, but with the body being studied as the heat source. After again measuring the heat received from the heat source $Q_{source}$, which remains the same as in the first experiment, and the heat $Q_{sink}$ given away to the heat sink, we can again write the ratio

$$\frac{Q_{source}}{Q_{sink}} = \frac{T_{source}}{T} \tag{6.63}$$

We thus have two equations (6.62) and (6.63) for determining the three quantities $T_{source}$, $T_{sink}$, and $T$. But we can also write a third equation determining the value of a degree:

$$T_{source} - T_{sink} = 100$$

These three equations are sufficient for determining the required temperature $T$ and the quantities $T_{source}$ and $T_{sink}$.

It remains to add that we could let our heat engine run in the opposite direction so that it would operate as a refrigerating machine. Here we would have to measure the quantity of heat transferred from the heat sink to the heat source and the magnitude of the external work spent to do this.

Of course, nobody ever measured the temperature in such an unusual way, and which is technically unrealizable. But there is no need to do this because the temperature scale established with the aid of a Carnot machine can be reproduced using a concrete substance with well-known properties. An ideal gas, for which we exactly know the equation of state, is such a substance, for instance. We have shown above that Eq. (6.61) is obtained if we use an ideal gas as the working body in a Carnot machine. It can be shown that the temperatures measured using the scale of a gas thermometer, where the temperature is obtained from the equation

$$T = \frac{pV}{R}$$

exactly coincide with the temperature that would have been found if the experiment described above were conducted.

It should be noted that the temperature scale based on the properties of a reversible Carnot machine is called the *thermodynamic temperature scale*. It was proposed by Kelvin after whom the scale was named. The temperatures measured using this scale are expressed in kelvins.

As regards the zero of the temperature scale, inspection of Eq. (6.18) shows that the temperature at which $Q_1 = 0$ should serve as zero. In this case, the efficiency of a Carnot machine equals unity and, therefore, there cannot be a lower temperature because the efficiency cannot exceed unity.

Since the thermodynamic temperature scale coincides with the scale of an ideal gas, then the zero of the Kelvin scale coincides with the absolute zero of temperature which we determined on a previous page. It should be noted in passing that according to the second law of thermodynamics the efficiency of a heat engine can never equal unity: the quantity of heat received from a heat source cannot be entirely converted into mechanical work. Therefore, the absolute zero of temperature also cannot be reached.

## 6.21. THE THIRD LAW OF THERMODYNAMICS

Numerous experiments show that with a decrease in the temperature a trend toward a greater degree of order is observed in any system. This is indicated by investigations of the structure of bodies, their magnetic properties, and many other data. It can be assumed that an ordered state corresponds to a lower energy of the particles forming a body, but that thermal motion prevents the establishment of order at high temperatures. If we could cool a body to absolute zero when thermal motion could not hinder the setting in of order, the maximum conceivable order would be established in a system, and the minimum entropy would correspond to this state.

The following question comes to our mind, however: how would a body behave at absolute zero if external work were done on it (for example if a pressure were applied to it)? Can the entropy of a body at absolute zero change?

On the basis of many experiments conducted at low temperatures, an important conclusion can be reached that is formulated as follows (W. Nernst, 1906): *at absolute zero of temperature any changes in state proceed without a change in the entropy.*

This statement is usually called *Nernst's theorem*. It is sometimes raised to the rank of the *third law of thermodynamics*.

We have seen above that the probabilistic interpretation of the concept of entropy permits us to arrive at the conclusion that the entropy at absolute zero of temperature equals zero, which naturally does not contradict Nernst's theorem.

It follows from the fact that the entropy also equals zero when $T = 0$ that absolute zero cannot be reached in principle: it is not difficult to show that if a body did exist with a temperature equal to zero, it would be possible

to construct a perpetual motion machine of the second kind. This contradicts the second law of thermodynamics. Sometimes the third law of thermodynamics is formulated as the *principle of unattainability of absolute zero.*

The third law of thermodynamics (we shall call it by this name) permits us to arrive at important conclusions concerning the behaviour of a substance at very low temperatures. It follows from it, for example, that with lowering of the temperature the heat capacity of bodies should tend to zero together with the temperature, and at absolute zero it should equal zero. This tendency is well confirmed by experiments. It can be shown that the coefficient of thermal expansion of bodies, the compressibility, and other quantities should tend to zero (and at $T = 0$ become equal to zero). All this, however, relates to systems in an equilibrium state. The entropy of bodies that are not in an equilibrium state may differ from zero at absolute zero of temperature.

## 6.22. NEGATIVE TEMPERATURES

If we proceed from the definition of the temperature that was given at the beginning of the book, i.e. that the temperature is proportional to the mean kinetic energy of particles, then the name of this section seems to be deprived of any meaning — kinetic energy cannot be negative! And for those atomic systems in which the energy contains only the kinetic energy of the motion of particles, a negative temperature actually does have no physical meaning.

But let us remember that in addition to the molecular-kinetic definition of the temperature, in Chap. 1 we also noted the part played by the temperature as a quantity determining the distribution of particles by energies (see Sec. 1.9). If we use this more general concept of temperature, we shall arrive at the possibility of the existence (at least in principle) of negative temperatures (i.e. temperatures below 0 K).

It can easily be seen that the Boltzmann equation (1.43), i.e.

$$\frac{n}{n_0} = \exp\left(-\frac{U}{kT}\right)$$

formally "permits" the temperature to take on not only positive, but also negative values.

Indeed, in this equation $n/n_0$ is the fraction of all the particles that are in a state having the energy $U$, and $n_0$ is the number of particles in a state with a certain initial energy from which the energy $U$ is counted. Inspection of the equation shows that the fraction of the particles $n/n_0$ having this energy diminishes with increasing $U$. For example when $U = kT$, the value of $n$ equals $n_0/e$ (here $e=2.71+$ is the base of natural logarithms). A considerably smaller number of particles have the energy $U = 2kT$ — in this

case $n = n_0/e^2$. It is clear that in an equilibrium state which we know the Boltzmann law to relate to, $n$ is always less than $n_0$.

Taking logarithms of Eq. (1.43), we get

$$\ln \frac{n}{n_0} = -\frac{U}{kT}$$

whence

$$T = -\frac{U}{k \ln \frac{n}{n_0}} \tag{6.64}$$

It can be seen from this expression for $T$ that if $n < n_0$, then $T > 0$.

If, however, an atomic system happened to exist in which $n$ could be *greater* than $n_0$, this would mean that the temperature can also take on negative values because $T$ becomes negative when $n > n_0$.

It will be easier for us to understand the circumstances in which this is possible if we consider not a classical system (in which a negative temperature cannot be realized), but a quantum one, and make use in addition of the concept of entropy: the latter, as we have just seen, is a quantity determining the degree of disorder in a system.

Suppose that a system is represented by a scheme of its energy levels (see for example Fig. 1, p. 18). At absolute zero of temperature, all the particles of our system are at their lowest energy levels, and all the remaining levels are vacant. A system in such conditions is ordered to the greatest possible degree, and its entropy equals zero (as does its heat capacity).

If we now raise the temperature of the system by supplying energy to it, particles will also pass to higher energy levels. The latter will thus also be partly populated, and the "population" of the higher energy levels will grow with increasing temperature. The distribution of the particles by energy levels is determined by the Boltzmann equation. Hence, it will be such that less particles will be at the higher levels than at the lower ones. The "settling" of the particles at many levels naturally increases the disorder in the system, and its entropy grows together with the temperature. The greatest disorder and, consequently, the maximum of the entropy would be achieved upon such a distribution of the particles by energies when they uniformly occupy all the energy levels. Such a distribution would mean that in Eq. (6.64) $n = n_0$ and, therefore, $T = \infty$. Hence, the uniform distribution of the particles by energies corresponds to an infinitely high temperature and a maximum entropy.

Such a distribution is impossible in the quantum system we are dealing with here because the number of levels is infinitely great while the number of particles is finite. Therefore, the entropy in such a system does not pass through a maximum, but grows monotonously with the temperature. At an infinitely high temperature, the entropy will also be infinitely great.

Now let us imagine such a system (a quantum one) in which there is an upper limit of its internal energy and the number of energy levels is finite. This is naturally possible only in a system where the energy does not include the kinetic energy of motion of the particles.

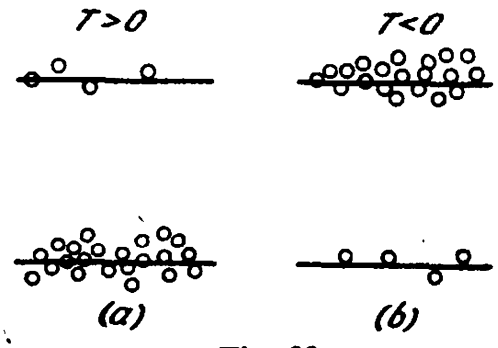


Fig. 99

In such a system at absolute zero of temperature, the particles will also occupy only the lowest energy levels, and the entropy will equal zero. A growth of the temperature is attended by the particles also "settling" at higher energy levels, causing a corresponding growth of the entropy. Figure 99*a* shows a system with two energy levels. But since the number of energy levels of the system, like the number of particles in it, is now finite, in the long run a state may be reached in which the particles are uniformly distributed among the energy levels. We have just seen that an infinitely high temperature and the maximum entropy correspond to this state. The energy of the system here will also be at a certain maximum, but will not be infinitely great. Hence, our old definition of the temperature as the mean energy of the particles can no longer be applied.

If we now impart additional energy in some way or other to the system that is already at an infinitely high temperature, the particles will pass over to a higher energy level, and this will result in the "population" of this high energy level becoming greater than that of the lower one (Fig. 99*b*). It is obvious that such an accumulation of the particles mainly at the high levels already points to certain order in comparison with the complete disorder that existed at $T = \infty$, i.e. upon the uniform distribution of the particles by energies. The entropy, which has reached its maximum at $T = \infty$, therefore begins to diminish upon a further supply of energy. But if the entropy decreases instead of increasing with a growth of the energy, this means that the temperature is not positive, but negative.

The more the energy supplied to the system, the greater will be the number of particles at the highest energy levels. In the limit, we can imagine a state in which all the particles will gather at the highest levels. Such a state is obviously also a quite ordered one. It is in no way "worse" than the one when all the particles occupy the lowest levels: in both cases there is complete order in the system, and the entropy equals zero. We can therefore designate the temperature at which this second quite ordered state sets in by $-0$, in contrast to the "conventional" absolute zero $(+0)$. The difference between these two "zeroes" is that we approach the first of them from the side of negative, and the second from the side of positive temperatures.

Thus, the conceivable temperatures of a system are not limited to the interval from absolute zero to infinity, but extend from $+0$ through $+\infty$,

$-\infty$ to $-0$, $+\infty$ and $-\infty$ coinciding with each other. Figure 100 depicts a curve showing how the entropy depends on the energy of a system. The part of the curve to the left of the maximum or peak corresponds to positive temperatures, and to the right of it to negative ones. The value of the temperature at the peak is $\pm\infty$.

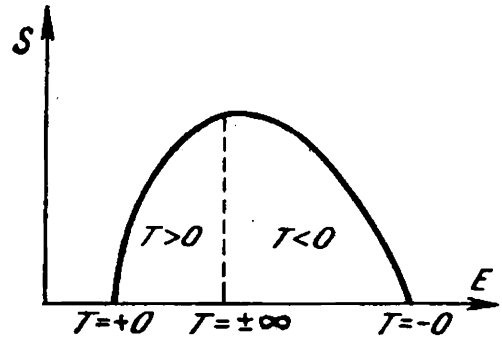


Fig. 100

From the viewpoint of orderliness and, consequently, of the entropy, the following three extreme states are therefore possible:

1. Complete order — the particles are concentrated at the lowest energy levels. This state corresponds to the "conventional" absolute zero (+0).

2. Complete disorder — the particles are uniformly distributed among all the energy levels. A temperature of $\pm\infty$ corresponds to this state.

3. Again complete order — the particles occupy only the highest energy levels. The temperature corresponding to this state is given the value of $-0$.

We have to do here, consequently, with a paradoxical situation: to arrive at negative temperatures, instead of cooling a system below absolute zero, which is impossible, we had to increase its energy, on the contrary. A negative temperature ($T < 0$) was found to be higher than an infinitely high temperature!

There is a very important difference between the two quite ordered states which we have just mentioned — states having temperatures of $+0$ and $-0$.

The state of "conventional" absolute zero, if it could be created in a system, would be retained in it for any length of time on condition that it is reliably isolated from the surroundings, i.e. isolated in the sense that no energy is supplied from the surroundings to the system. This state is one of stable equilibrium from which the system by itself, without any outside interference, cannot emerge. The explanation is that the energy of the system in this state has a minimum value.

On the other hand, the state of the negative absolute zero is an extremely non-equilibrium state because the energy of the system is maximum. If it were possible to bring a system up to this state and then leave it alone, it would immediately pass out of this non-equilibrium, unstable state. It could be retained only by continuously supplying energy to the system. Without this, the particles at the higher energy levels would "drop" without fail to the lower levels.

A common property of both "zeroes" is their unattainability: an infinitely great amount of energy must be spent to reach them.

It must be noted that unstable and non-equilibrium states include not only that corresponding to a temperature of $-0$, but also all states with negative temperatures. Values of $n > n_0$ correspond to all of them whereas for equilibrium we must have the reverse relationship of these quantities.

We have already noted that negative temperatures are higher than positive ones. Therefore, if we bring a body heated (we cannot say cooled) to negative temperatures into contact with a body whose temperature is positive, then energy will pass from the former to the latter, and not conversely. This means that its temperature is higher even if it is negative. Upon the contact of two bodies having negative temperatures, energy will pass from the body with the lower absolute value of the temperature to the body with the higher absolute value of it.

Being in a state of extreme non-equilibrium, a body heated to a negative temperature gives up its energy very readily. Therefore, to provide the possibility of creating such a state, the system must be reliably isolated from other bodies (at any rate from systems that are not similar to it, i.e. that do not have a finite number of energy levels).*

A state having a negative temperature, however, is out of equilibrium to such an extent that even if a system in this state is isolated and cannot give up its energy to another system, it can nevertheless give away energy in the form of radiation until it transfers to a state (equilibrium) with a positive temperature.

It remains to add that atomic systems having a limited set of energy levels in which, as we have seen, a state with a negative temperature can be realized is not only a mental theoretical construction. Such systems actually exist, and a negative temperature can actually be obtained in them. The radiation obtained in the transition from a state with a negative temperature to a state with a conventional one is used in practice in special instruments: molecular generators and amplifiers — masers and lasers. But space does not permit us to stop here and treat this question in greater detail.

---

*It was shown in an earlier section that the concept of temperature is integrally related to equilibrium. Therefore, strictly speaking, in the case being considered we can only formally speak of the temperature. It should be remembered that the Boltzmann equation also gives an equilibrium dist ribution of particles by energies.

CHAPTER 7

# PROPERTIES OF LIQUIDS

Our consideration of the properties of gases at increased pressures when they cannot be considered ideal led us to the conclusion that the properties of liquids should also not differ appreciably from them. This already follows from the fact of the existence of a critical temperature at which the difference between a liquid and its vapour disappears, and from the resulting possibility of the continuous transition from the gaseous to the liquid state. The equation of state for real gases in accordance with its inherent meaning describes both the gaseous and the liquid states, as well as the transition between them. Everything seems to point to the circumstance that there is only a quantitative difference in density between a liquid and a gas. And the use of the term "fluid" denoting both a liquid and a gas shows that they have common properties.

This is true to a certain extent. But the quantitative difference between a liquid and a gas is so great (their densities far from the critical temperature differ almost a thousand times) that the behaviour and the properties of liquids and gases are found to differ also qualitatively.

The main features of a liquid are its ability to retain its volume (unlike gases, the volume of a liquid is not determined by that of the vessel containing it) and its having a free surface.

We already know that the van der Waals equation is approximate and cannot be used for such accurate calculations of various phenomena as could be done for ideal gases with the aid of the Clapeyron equation. Some properties of liquids, however, can be considered, at least qualitatively, on the basis of an equation of state. They include, for example, thermal expansion and compressibility. We shall begin our treatment of liquids and their properties with these phenomena involving the volume. Next we shal

consider other bulk properties of liquids and compare them with the corresponding properties of gases. After this we shall consider surface phenomena, i.e. phenomena due to liquids having a free surface.

## 7.1. BULK PROPERTIES OF LIQUIDS

Let us first consider the properties of liquids that can be studied directly from the equation of state, namely, the compressibility and thermal expansion.

**Compressibility of Liquids.** By the *compressibility* $\varkappa$ of a body is meant the relative change in the volume $dV$ when the pressure $p$ changes by one unit, i.e. the quantity

$$\varkappa = \frac{1}{V}\frac{dV}{dp} \tag{7.1}$$

For ideal gases, as was shown in Chap. 1 [see Eq. (1.14)],

$$\varkappa = -\frac{1}{p}$$

so that, for instance, when $p = 1$ atm we have $\varkappa = -1$ atm$^{-1}$: when the pressure increases from one to two atmospheres the volume of a gas is halved.

The compressibility of liquids, unlike gases, is very low. This can be seen immediately when looking at a curve of the van der Waals equation (Fig. 101). Here section $AB$ corresponds to the liquid state. The steepness of this section indicates that the derivative $dV/dp$ and, therefore, the compressibility is very low: a very great change in pressure is needed for an insignificant change in volume.

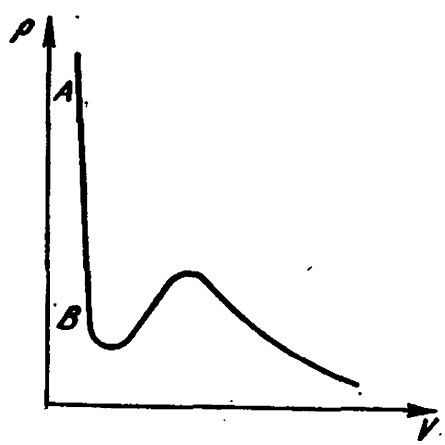


Fig. 101

Experiments show that the compressibility of liquids is indeed very low and for most of them ranges from $10^{-4}$ to $10^{-5}$ atm$^{-1}$. Consequently, the compressibility of gases is tens and hundreds of thousands of times greater than that of liquids. Of all liquids, liquid helium has the greatest compressibility: at a pressure of several atmospheres the compressibility $\varkappa$ equals $8\times10^{-3}$ atm$^{-1}$ for it. The compressibility of water is $4.53\times\times10^{-5}$ and of mercury $-3.95\times10^{-6}$ atm$^{-1}$.

The compressibility depends on the pressure and diminishes when the latter grows. This is to be expected because compression of a liquid is attended by a reduction in the distance between its particles and an increase in the forces of repulsion between them which makes further approach of

the particles more difficult. It should be noted that whereas at conventional pressures the compressibilities of various liquids may greatly differ from one another, at very high pressures the compressibilities of all liquids are almost the same.

The compressibility of a liquid depends on the temperature. We know that in heating the volume of a liquid grows owing to thermal expansion and the distances between the molecules increase. As a result, the forces of repulsion between the molecules diminish, and it becomes easier to compress the liquid. This is why the compressibility grows with increasing temperature. Elevation of the temperature therefore acts in the opposite way to an increase in the pressure (this, by the way, relates not only to liquids and not only to their compressibility).

The features of compressibility which we have just described can be obtained directly from the van der Waals equation. Since this equation relates the pressure, volume, and temperature, it can be used to calculate the quantity $(1/V)\ (dV/dp)$ that determines the compressibility [see Eq. (7.1)]. It is only necessary to remember in calculations that the constants $a$ and $b$ in the equation of state are actually not constants, but depend on the temperature (the constant $b$ also depends on the specific volume of a substance), and the form of this relationship can be determined only from experimental data. A complex of experimental data made it possible to obtain the following empirical formula for the compressibility of a liquid:

$$\varkappa = \frac{A}{V(p + p_T)} \qquad (7.2)$$

where $A$ = function increasing with the temperature
$p$ = external pressure
$p_T$ = pressure connected with the van der Waals forces $(a/V^2)$ at the temperature $T$.

Equation (7.2) shows that the compressibility does indeed grow with increasing temperature and diminish with increasing pressure. This equation is an approximate one suitable for a comparatively limited region of pressures.

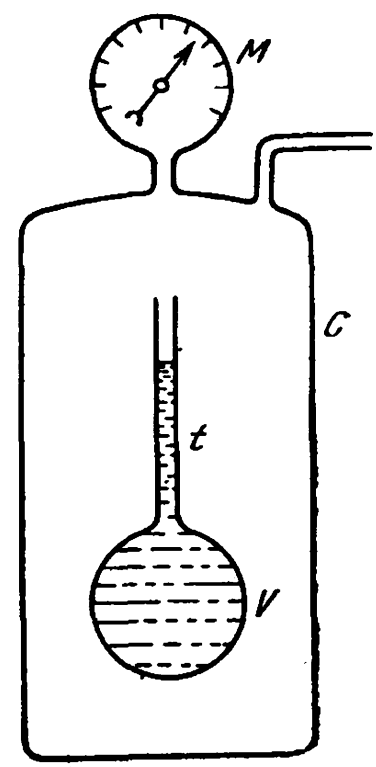


Fig. 102

**Experimental Determination of the Compressibility of a Liquid.** Instruments and apparatuses used to measure the compressibility are called *piezometers*. A very simple piezometer that can be used to measure the compressibility of a liquid at not very great pressures is shown schematically in Fig. 102. The liquid being studied is poured into vessel $V$ so that it also enters narrow tube (capillary) $t$. The vessel, in turn, is placed in chamber $C$ in which an increased pressure

measured by manometer $M$ can be created. Since the same pressure acts on the walls of vessel $V$ containing the liquid from outside and inside, the volume of the vessel does not change as a result of the application of an external pressure (this condition must always be observed when measuring the compressibility).

The applied pressure causes the volume of the liquid in vessel $V$ to diminish somewhat, and this reduction becomes noticeable as a result of lowering of the level in capillary $t$. Owing to the small value of the compressibility of a liquid, it would be impossible to note the change in the volume in the vessel without the capillary.

If the cross-sectional area of the capillary is $A$, and the level of the liquid in it lowered by the value $\Delta h$, then the change in the volume equals $A\,\Delta h$. Knowing the initial volume of the liquid and reading the pressure change on the manometer, we can calculate the compressibility by Eq. (7.1).

**Thermal Expansion of a Liquid.** The thermal expansion of a substance is characterized by the cubic expansion coefficient

$$\alpha = \frac{1}{V}\frac{dV}{dT} \tag{7.3}$$

i.e. by the relative change in the volume $V$ when the temperature $T$ changes by one kelvin.

We showed in Chap. 1 that for ideal gases $\alpha = 1/T$. At the melting point of ice ($T = 273$ K), therefore, $\alpha = 1/273 = 3.66\times10^{-3}$ K$^{-1}$ for an ideal gas. The numerical value of the cubic expansion coefficient is much lower for liquids and depends on the temperature to a somewhat smaller extent.

Table 15 gives the values of $\alpha$ for selected liquids at room temperature.

*Table 15*

**Cubic Expansion Coefficient for Selected Liquids at Room Temperature**

| Substance | $\alpha$, K$^{-1}$ | Substance | $\alpha$, K$^{-1}$ |
|---|---|---|---|
| Ethyl alcohol | $1.1\times10^{-3}$ | Glycerine | $5.3\times10^{-4}$ |
| Ether | $1.63\times10^{-3}$ | Mercury | $1.8\times10^{-4}$ |
| Olive oil | $7.2\times10^{-4}$ | Water (at 15 °C) | $1.5\times10^{-4}$ |
| Water (at 90 °C) | $7.0\times10^{-4}$ | | |

It follows from what has been said above about the action of the pressure and the temperature that the cubic expansion coefficient must diminish with increasing pressure (which naturally prevents expansion) and grow with increasing temperature.

The phenomenon of thermal expansion, like compressibility, can be considered on the basis of the van der Waals equation of state from which the

value of the quantity $dV/dT$ determining the coefficient $\alpha$ can be obtained (see Chap. 8).

We shall note here that it follows from the law of corresponding states that the cubic expansion coefficient must be the same for all liquids at identical reduced temperatures. The same relates to the compressibility. Experiments give an excellent confirmation of this conclusion (better than of other corollaries of the van der Waals equation).

**Relationship Between the Compressibility and the Cubic Expansion Coefficient.** On the basis of the most general considerations, even without knowing the form of the equation of state of a substance, we can establish relationships between the following quantities:

(1) $(\partial V/\partial T)_p$ — the change in the volume of a body per unit change in temperature at constant pressure (thermal expansion);

(2) $(\partial V/\partial p)_T$ — the change in the volume of a body per unit change in pressure at constant temperature (compressibility);

(3) $(\partial p/\partial T)_V$ — the change in pressure per unit change in temperature at constant volume of a body (thermal stress).

That a relationship must exist between these quantities is clear from the following considerations. If a body subjected to heating expands, i.e. increases its volume $V$, it can be compressed to its initial volume by increasing the external pressure $p$. Hence, the volume can be kept constant by simultaneously increasing the temperature and the pressure. It is easy to understand that the increase in pressure per unit of growth in temperature, $\partial p/\partial T$, needed to compensate for the increase in volume due to this change in temperature is the greater, the bigger is the value of the thermal expansion $\partial V/\partial T$ and the smaller the compressibility of a body $\partial V/\partial p$. It is exactly this condition that determines the relationship between the three quantities indicated above.

Let us attempt to establish this relationship quantitatively. The relationship between the pressure, volume, and temperature is determined by the equation of state

$$p = f(V, T) \tag{7.4}$$

No matter what the form of relationship (7.4) is, we can affirm that if a body is transferred from the state determined by the quantities $V$ and $T$ to an infinitely close state with the values of the volume and the temperature equal to $V + dV$ and $T + dT$, then the pressure $dp$ due to this change does not depend on how this change in state was achieved. This means that

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{7.5}$$

is a total differential, i.e. the total change in the pressure equals the sum of the changes in the pressure due to the change in the volume and the change in the temperature taken separately.

We shall remind the reader again that at a constant temperature ($dT = 0$) the change in the pressure is opposite in sign to the change in the volume. If the volume remains constant ($dV = 0$), then the sign of the change in the pressure coincides with that of the change in the temperature.

If we select the ratio of the change in the volume $dV$ to the change in the temperature $dT$ so that the pressure remains constant, i.e. so that $dp = 0$, then this ratio according to the definition of a partial derivative must be written in the form $(\partial V/\partial T)_p$. Hence from Eq. (7.5), it identically follows (at $dp = 0$) that

$$\left(\frac{\partial V}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} \tag{7.6}$$

or, taking into account that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial p}\right)_V}$$

we get the following symmetrical identity:

$$\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial T}{\partial p}\right)_V \equiv -1 \tag{7.7}$$

This is the quantitative expression of the relationship between the quantities of interest to us.

This relationship naturally holds for all bodies.

Let us rewrite Eq. (7.7) so that it includes the experimentally measured cubic expansion coefficient $\alpha$ and the compressibility (isothermal) $\varkappa$:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad \varkappa = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

We get

$$\alpha V \frac{1}{\varkappa V}\left(\frac{\partial T}{\partial p}\right)_V = -1$$

or

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\alpha}{\varkappa} \tag{7.8}$$

Equation (7.8) shows that if we change the temperature of a liquid (or of any substance) at a constant volume, the change in the pressure caused by a change in the temperature of one kelvin equals the ratio of the cubic expansion coefficient to the compressibility.

If, for instance, a soldered tube is completely filled with mercury, then when the temperature is changed by one kelvin the pressure changes by the amount $\Delta p$ equal to $\alpha/\varkappa$ (the cubic expansion coefficient of the solid material of the tube is considerably lower than that of mercury so that we may disregard the change in the volume of the tube). For mercury, $\alpha = 1.8 \times 10^{-4}$, and $\varkappa = -3.95 \times 10^{-6}$. Consequently, $\Delta p = 46.5$ atm, i.e. a quite considerable pressure is developed. This, particularly, explains why we must never heat a mercury thermometer so much that the mercury upon expanding will fill the entire volume of the capillary—upon a further even negligible increase in the temperature the capillary will be destroyed.

It follows from Eq. (7.8) that if we know the cubic expansion coefficient of a liquid, then we can also determine the compressibility. For this purpose, it is possible, for example, to use the device shown schematically in Fig. 103. The liquid being studied is poured into a vessel provided with a thin tube, and the vessel is placed in a heater that can be used to change the temperature of the liquid. The tube is connected to a cylinder with a compressed gas (nitrogen or argon to prevent chemical changes of the liquid). Upon heating, the level of the liquid in the tube should rise owing to thermal expansion, but this rise is compensated by an increase in the pressure over the liquid. We measure the change in the temperature of the liquid with thermometer $t$ and the change in the pressure that keeps the level of the liquid in the tube constant with manometer $M$. Using the results obtained in Eq. (7.8), we calculate the compressibility.

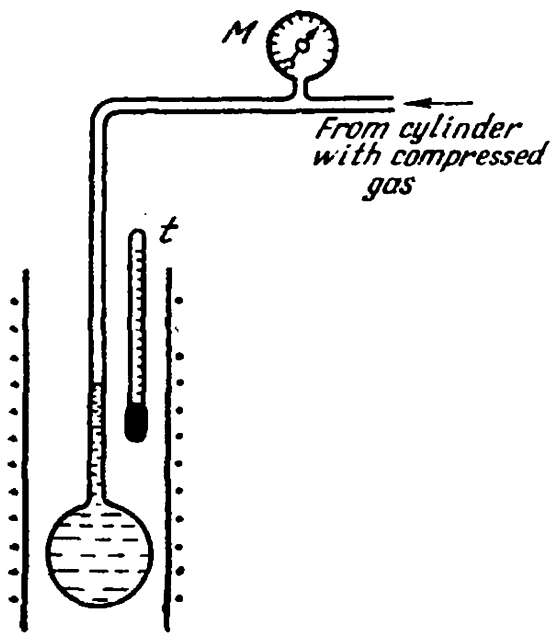



Fig. 103

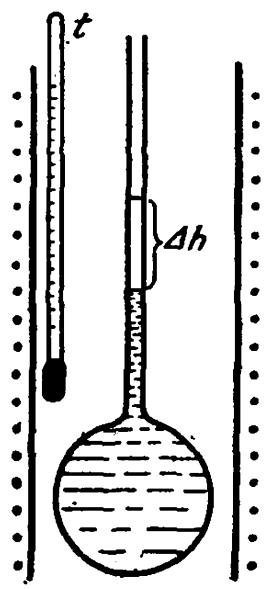



Fig. 104

**Experimental Determination of the Cubic Expansion Coefficient of a Liquid.** Instruments intended for measurement of the cubic expansion coefficient of bodies are called *dilatometers*. The simplest method used in dilatometry consists in the following.

The liquid being studied is placed in a vessel with a thermometric tube so that the liquid also fills part of the tube. If the temperature of the liquid is raised with the aid of a heater which the vessel is placed in (see Fig. 104), its level will rise by $\Delta h$ as a result of thermal expansion. Using thermometer $t$ to measure the change in the temperature $\Delta t$ and knowing the initial volume $V_0$ of the liquid, we can calculate the cubic expansion coefficient by the equation

$$\alpha = \frac{1}{V_0}\frac{\Delta V}{\Delta t} = \frac{A\,\Delta h}{V_0\,\Delta t} \tag{7.9}$$

where $A$ is the cross-sectional area of the tube. The initial volume $V_0$ of the liquid is easily found according to its mass $M$ and density $\rho$:

$$V_0 = \frac{M}{\rho}$$

The cross-sectional area of the tube is also determined according to the mass of the liquid of a known density filling a definite part (with the length $L$) of the tube:

$$A = \frac{M}{\rho L}$$

The above method is not distinguished by a high accuracy, first of all because it takes no account of the change in the volume of the vessel containing the liquid. Therefore, the corresponding correction must be introduced when using this method.

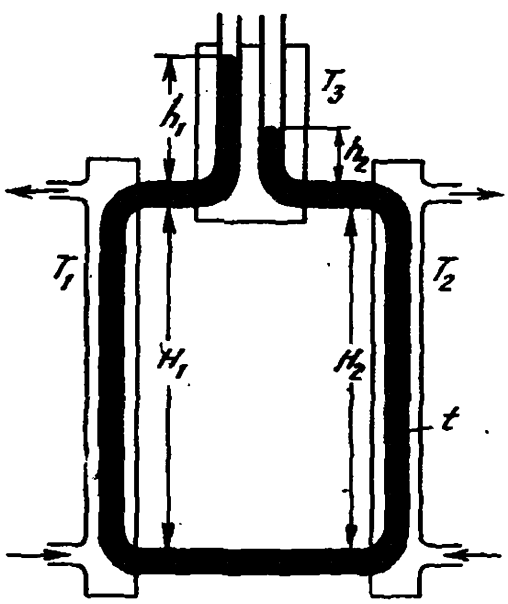


Fig. 105

This shortcoming is absent in another method of determining the cubic expansion coefficient—the classical method proposed by P. Dulong and A. Petit and improved by H. Regnault. This method is based on using the equilibrium of two columns of liquid in communicating vessels when the liquids in them have different temperatures. In this case, the heights of the columns are inversely proportional to the densities of the liquid in them.

A schematic view of the instrument used is shown in Fig. 105. The liquid being studied is poured into tube $t$ having the shape shown in the figure. The open ends of the tube are brought together to facilitate the determination of the difference between the levels. Both vertical limbs of the tube are placed in thermostats $T_1$ and $T_2$. These are vessels through which water having a preset temperature is

passed. These "jacket" vessels make it possible to establish the required temperature difference of the liquid in the two limbs of the tube. As a result, the densities of the liquid in them will also be different. The ends of the tube are placed in thermostat $T_3$ which ensures that they both have the temperature of the colder limb.

In our figure, as can be seen from the difference between the levels, the right-hand limb (in thermostat $T_2$) is colder than the left-hand one. We shall assume for simplicity that the heights of both limbs are the same so that $H_1 = H_2 = H$.

Bearing in mind that the pressure of a column of liquid equals the product of the density of the liquid, the acceleration of free fall $g$, and the height of the column, we can write that the difference between the pressures in the vertical limbs is $H(\rho_2 - \rho_1)\, g$, where $\rho_1$ and $\rho_2$ are the densities of the liquid in the right-hand (cold) and left-hand (warm) limbs, respectively. This pressure difference is balanced by the difference in levels $h_1 - h_2$. As a result, the pressure difference $(h_1 - h_2)\, g\rho_2$ appears. We can therefore write the obvious equation

$$H(\rho_2 - \rho_1) = (h_1 - h_2)\, \rho_2 \tag{7.10}$$

The volume of the liquid at a certain temperature $t$ is related to the volume $V_0$ of the same liquid at a different temperature $t_0$ by the well-known expression

$$V_t = V_0(1 + \alpha\, \Delta t) \tag{7.11}$$

where $\Delta t = t - t_0$

$\alpha$ = cubic expansion coefficient.

When applied to our case, this equation becomes

$$V_{t_1} = V_{t_2}(1 + \alpha\, \Delta t)$$

or

$$\frac{V_{t_1}}{V_{t_2}} = 1 + \alpha\, \Delta t$$

where $t_1$ and $t_2$ = temperatures of the left-hand and right-hand limbs

$$\Delta t = t_1 - t_2.$$

The ratio of the densities of the liquid in the two limbs is naturally inversely proportional to the ratio of the volumes. Hence,

$$\frac{\rho_1}{\rho_2} = \frac{1}{1 + \alpha\, \Delta t} \quad \text{or} \quad \rho_1 = \frac{\rho_2}{1 + \alpha\, \Delta t}$$

Using this value of $\rho_1$ in Eq. (7.10), we get

$$H - \frac{H}{1 + \alpha\, \Delta t} = h_1 - h_2$$

whence we get the following expression for $\alpha$:

$$\alpha = \frac{h_1 - h_2}{[H - (h_1 - h_2)]\,\Delta t} \tag{7.12}$$

Thus, to determine $\alpha$, we must carefully measure the difference between the levels $h_1 - h_2$, the height of the columns $H$, and the temperature difference $\Delta t$. Strict equality of the heights of both limbs must be ensured in the measurements. Experimental installations usually have a special device that can be used to regulate the values of the heights $H_1$ and $H_2$. It is also possible, however, to make measurements when the heights of the vertical limbs of the tube are not equal. In this case, $\alpha$ is determined by the expression

$$\alpha = \frac{(H_1 - H_2) - (h_1 - h_2)}{[H_2 + (h_1 - h_2)]\,\Delta t} \tag{7.13}$$

Since the pressure of a column of liquid depends only on its height and on the density of the liquid, but does not depend on its diameter, no correction has to be introduced for thermal expansion of the material of the tube.

**Anomaly of Water.** Most liquids, like other bodies, increase their volume when the temperature rises, thus reducing their density. Water differs in having a well-known anomaly consisting in that in the region of temperatures from 0 to 4 °C elevation of the temperature causes the volume to diminish instead of growing so that at 4 °C water has the maximum density.

The explanation of this anomaly is that the molecules of water partly *associate*, i.e. gather into groups of several molecules and form peculiar large molecules. Water evidently consists of three kinds of molecules corresponding to the formulas $H_2O$, $(H_2O)_2$, and $(H_2O)_3$ whose specific volume is different. At different temperatures, the ratio of the concentrations of these groups of molecules is different. This is exactly why the specific volume of water has a minimum value at a definite temperature (4 °C).

Liquid helium has an anomaly that is similar in nature. Its density is the greatest at 2.186 K. Here, however, the anomaly is explained by the fact that at the temperature of the maximum density liquid helium undergoes a phase transition so that above and below this temperature we have two different phases of liquid helium. They are called He I and He II (see Chap. 8), and their properties, as we shall see on a later page, strikingly differ from each other. It is interesting to note that liquid helium is the only liquid in nature in which a phase transition occurs.

## 7.2. HEAT CAPACITY OF LIQUIDS

The simple laws that were obtained for the heat capacities of ideal gases from the equations of the kinetic theory cannot hold for liquids (as for real gases) because their internal energy is determined not only by the ki-

netic energy of the thermal movements of the molecules, but also by their potential energy of interaction.

Experiments show that the heat capacity of liquids depends on the temperature, the form of the relationship varying for different liquids. The heat capacity of most liquids increases with a growth in the temperature, but in certain others (mercury) it diminishes. The heat capacity of some liquids first drops with a growth in the temperature and then, after passing through a minimum, begins to grow. The heat capacity of water changes in this way (this is another one of its numerous anomalies).

The heat capacity at constant volume and at constant pressure should be distinguished in liquids, as in gases. The difference between the molar heat capacities $C_p - C_V$ equals, of course, the work of expansion $p\,dV$ ($p$ is the molecular pressure) of a mole of the liquid when it is heated by one degree, therefore the numerical value of this difference depends on the value of the cubic expansion coefficient of the liquid. Unlike ideal gases, the value of $C_p - C_V$ for liquids does not equal the molar constant $R$, but may be either greater or smaller than it depending on the value of $\alpha$ and on the magnitude of the internal forces of interaction of the molecules of the liquid against which the work of expansion is being done (the pressure $p$ in the expression $p\,dV$ is connected with exactly these forces).

For example for liquid argon at 140 K, the heat capacity $C_p = 15.4$ cal/mol·K while $C_V = 4.65$ cal/mol·K and, therefore, the difference between the heat capacities $C_p - C_V = 10.75$ cal/mol·K. For water, however, at a temperature of about 0 °C, the heat capacity $C_p = 18.1$ while $C_V = 18.09$ cal/mol·K, so that $C_p - C_V = 0.01$ cal/mol·K.

Thus, the heat capacity of liquids cannot be expressed by such simple formulas as that of ideal gases. The heat capacities may have the most diverse numerical values. An exception are liquid metals for which the molar heat capacity is usually close to the value of $3R \approx 6$ cal/mol·K.

## 7.3. TRANSPORT PROCESSES IN LIQUIDS

Diffusion, thermal conductivity, and viscosity are observed in liquids, as in gases. But the mechanism of these processes is different in liquids than in gases.

Transport processes in gases are determined by the free path of molecules. This is why the expressions for all the transport coefficients contain the free path as a factor. But in liquids, as in very dense gases, the concept of the free path loses its meaning. In liquids, the mean distance between molecules is of the same order of magnitude as the dimensions of the molecules themselves, and therefore the molecules have no "free" path. The molecules of a liquid can only slightly oscillate within the confines of the intermolecular distances.

From time to time, however, an oscillating molecule as a result of fluctuation may receive from the neighbouring molecules a surplus energy sufficient to perform a jump over a certain distance $\delta$. The molecule will oscillate for some time at its new place until it again receives the energy needed for a jump as a result of fluctuation. It again performs a jump, and so on. It is exactly these oscillations alternating with jumps that form the thermal movements of the molecules of a liquid.

How often do the molecular jumps occur? How much time elapses between jumps? This depends on the properties of the molecules, on the forces of interaction between them, and on the density of the liquid. Although the forces of interaction between molecules are of a very intricate nature, we can nevertheless indicate some considerations on the movements of molecules and the transport processes related to them.

Fick's law (see Sec. 3.6) remains true for *diffusion* in a liquid, as in any substance. An expression for the diffusion coefficient $D$ can be obtained from the following considerations.

If the time between the jumps of molecules (it can be called the time of the "settled" life of a molecule) is denoted by $t$, then the quantity $\delta/t$ is the velocity of a molecule. This allows us to ompare $\delta$ with the mean free path, and $\delta/t$ with the mean velocity of a molecule. Hence, by analogy with ideal gases for which the diffusion coefficient is determined by the product of the free path and the mean velocity of the molecules [see Eq. (3.19)], we can also write for a liquid that the diffusion coefficient (more precisely the self-diffusion coefficient) is expressed by the equation

$$D = \frac{1}{6}\delta\frac{\overline{\delta}}{\overline{t}} = \frac{1}{6}\frac{\overline{\delta^2}}{\overline{t}} \tag{7.14}$$

The factor 1/6 (instead of 1/3) appears here because the movements of the molecules have the nature of random wandering for which six directions are equally possible (three axes of coordinates and two directions along each of them) so that one-sixth of all the molecules travel in a certain selected direction. For reasons which we explained when considering Brownian motion (see Sec. 1.7), Eq. (7.14) includes the mean value of the square $\overline{\delta^2}$, and not the square of the mean value $(\overline{\delta})^2$.

The coefficient of self-diffusion $D$ depends greatly on the temperature first of all because elevation of the latter is attended by diminishing of the duration $t$ of the "settled" life of a molecule, and this results in a sharp increase in $D$ with the temperature. The time spent by a molecule at a given place in a liquid is determined by the probability of it receiving the energy $E_a$ sufficient for a jump. And this probability, as always in such cases, is expressed by the Boltzmann law [see Eq. (1.43)]:

$$\frac{n}{n_0} = \exp\left(-\frac{E_a}{kT}\right)$$

Here $n$ is the number of molecules in a unit volume whose energy equals $E_a$, and $n_0$ is the number of molecules in the same volume whose energy is of the order of magnitude of the mean thermal energy, i.e. $kT$. The greater the probability of a molecule receiving the energy $E_a$, the smaller will be the duration of its "settled" life $\bar{t}$. We can therefore write the following expression for the mean time $\bar{t}$:

$$\bar{t} = A \exp\left(\frac{E_a}{kT}\right) \tag{7.15}$$

The factor $A$ has a clear physical meaning. Before a molecule performs a jump, it oscillates with a certain frequency $\nu$. Each oscillation can be considered as an "attempt" of a molecule to perform a jump. Hence, the probability of performing it is the greater, and the settled life of a molecule is the smaller, the greater is the frequency of oscillations $\nu$. The factor $A$ is related to this frequency, i.e. $A = 1/\nu$. Consequently, the factor $A$ has the meaning of the period of oscillations of a molecule.

If we introduce Eq. (7.15) into Eq. (7.14) for the diffusion coefficient, we get:

$$D = B \exp\left(-\frac{E_a}{kT}\right) \tag{7.16}$$

where $B = \frac{1}{6}\overline{\delta^2}\nu$

$E_a$ = energy needed for a jump of a molecule, called the *activation energy* of a molecule.

The numerical value of the diffusion coefficient for liquids is much smaller than for gases. For example, the diffusion coefficient of NaCl in water at room temperature is $1.1 \times 10^{-9}$ m$^2$/s whereas for the diffusion of argon into helium it is $7 \times 10^{-5}$ m$^2$/s.

*Internal friction (viscosity)* appears in liquids, as in gases, upon motion of a liquid owing to transfer of the impulse (momentum) in a direction at right angles to the direction of motion. The impulse transfers from one layer to another upon the jumps of the molecules mentioned above. The general law of internal friction is Newton's law which we have already become acquainted with in Sec. 3.14. The viscosity $\eta$ (the coefficient of internal friction) can be obtained on the basis of the same considerations on the movements of molecules which we have already given. A liquid will obviously be the more fluid (the less viscous), the smaller is the time $\bar{t}$ of the "settled" life of the molecules and, consequently, the more frequent are the jumps. These considerations lead to an expression for the viscosity called the *Frenkel-Andrade equation:*

$$\eta = C \exp\left(\frac{E_a}{kT}\right) \tag{7.17}$$

The factor $C$ in this equation depends on the length of a jump $\delta$, the frequency of oscillations $\nu$, and the temperature. The temperature dependence of the viscosity, however, is determined by the factor $\exp(E_a/kT)$. It follows from this equation that the viscosity rapidly diminishes with increasing temperature. Thus, the viscosity of water when the temperature changes from 0 to 100 °C diminishes from $1.8 \times 10^{-3}$ to $2.8 \times 10^{-4}$ kg/m·s.

The numerical values of the viscosity of selected liquids at room temperature can be assessed according to the data of Table 16.

*Table 16*

**Viscosity (Coefficient of Internal Friction) of Selected Liquids**

| Substance | $\eta \times 10^3$, kg/m·s | Substance | $\eta \times 10^3$, kg/m·s |
|---|---|---|---|
| Ether | 0.23 | Sulphuric acid | 22 |
| Petrol | 0.65 | Glycerine | 830 |
| Water | 1 | Castor oil | 986 |
| Ethyl alcohol | 1.19 | | |

*Thermal conductivity* occurs in liquids, as in gases, when a temperature gradient is present. If in gases, however, energy is transferred upon collisions of the particles performing translational motion, then in liquids energy is transferred upon the collisions of oscillating particles. The particles having a higher energy oscillate with a greater amplitude and upon collisions with other particles swing them, as it were, transmitting energy to them. Such a mechanism of energy transfer, like the one acting in gases, does not ensure its rapid transfer, and therefore the thermal conductivity of liquids is very low, although it is several times greater than that of gases.

For instance, the thermal conductivity of ethyl alcohol equals 1.76 W/m·K, and of air (at 1 atm) equals 0.23 (in the same units). An exception are liquid metals whose coefficients of thermal conductivity are close to the values for the solid metals. The explanation is that in liquid metals heat is transferred not only together with the transfer of oscillations from particle to particle, but also with the aid of mobile electrically charged particles—electrons, which are present in metals, but absent in other liquids.

**Experimental Determination of the Viscosity of Liquids.** Instruments used for measuring the viscosity are called *viscosimeters*. A great variety of these instruments are in use. Measurements in most of them are based on observing the outflow of a liquid through capillaries, the velocity of the

outflow depending on the viscosity according to the well-known Poiseuille equation

$$V = \frac{\pi r^4}{8\eta} \frac{\Delta p}{L} \tag{7.18}$$

where $V$ is the volume of liquid flowing in a unit time through a capillary of the radius $r$ under the action of the pressure difference $\Delta p$ with the length of the capillary equal to $L$.

Some viscosimeters measure the velocity of dropping of a ball in the liquid being studied to determine $\eta$. The velocity of dropping $v$ is related to the viscosity $\eta$ by the equation

$$v = \frac{2}{9} \frac{\rho_1 - \rho_2}{\eta} gr^2 \tag{7.19}$$

where $r$ = radius of the ball
$\rho_1$ = its density
$\rho_2$ = density of the liquid
$g$ = acceleration of free fall.

Equation (7.19) is easily obtained from the Stokes formula (see p. 45).

Finally, many viscosimeters use the attenuation of the oscillations of a disk or a cylinder in the liquid being studied as the phenomenon related to the viscosity.

In all cases of measuring the viscosity, the velocity of the liquid itself or of bodies moving relative to it must be low to prevent eddies from forming in the liquid. This is the reason why capillaries are used.

A capillary viscosimeter that is often employed is shown schematically in Fig. 106. It is a U-shaped tube into one of whose limbs capillary $C$ is soldered. The upper end of the capillary opens up into reservoir $R_1$. The other limb is an ordinary (not capillary) tube also provided with reservoir $R_2$ at its lower end. Before an experiment, the liquid is poured into reservoir $R_2$ and is then sucked into reservoir $R_1$. After this, the liquid is allowed to flow under the action of its weight, and the time is measured during which the level of the liquid will lower from mark $m_1$ to mark $m_2$ (see Fig. 106). Knowing the density of the liquid and the dimensions of the viscosimeter, we can determine the viscosity.

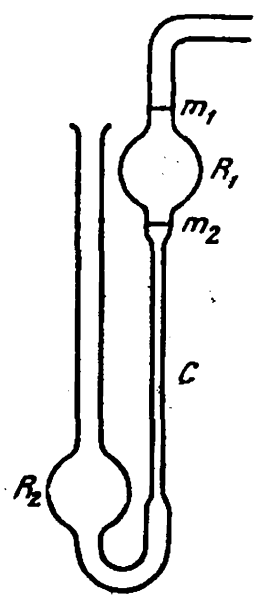


Fig. 106

Relative measurements of the viscosity are especially simple: here the liquid being studied is compared with a liquid whose viscosity is well known. It is only necessary to measure the time required for each liquid to flow from $m_1$ to $m_2$.

## 7.4. PHENOMENA ON THE BOUNDARY OF A LIQUID

**Surface Tension.** The surface of a liquid in contact with another medium, for instance with its own vapour, with another liquid, or with a solid body (particularly, with the walls of the vessel in which it is contained) is in special conditions in comparison with the remaining part of the liquid.

These special conditions appear because the molecules of the boundary layer of the liquid, unlike the molecules in its bulk, are not surrounded on all sides by molecules of the same liquid. Part of the "neighbours" of the surface molecules are particles of the second medium in contact with the liquid. This medium may differ from the liquid both in the nature and the density of its particles. Having different neighbours, the molecules of the surface layer interact with them differently. Therefore, the forces acting on each molecule in this layer are not balanced — there is a certain resultant force directed either toward the bulk of the liquid or toward the bulk of the neighbouring medium. As a result, movement of a molecule from the surface layer into the bulk of the liquid or into the bulk of the neighbouring medium is attended by the performance of work (the molecules in the bulk of a liquid which are surrounded on all sides by their like are in equilibrium and their movement does not require any work to be done). The magnitude and the sign of this work depend on the relationship between the forces of interaction of the molecules of the surface layer with their like and with molecules of the second medium.

If a liquid has an interface with its own vapour (saturated), i.e. if we have to do with *one* substance, the force which the molecules of the surface layer are subjected to is directed *into* the liquid. The explanation is that the density of the molecules in the liquid is much greater than in the saturated vapour over it (far from the critical temperature), and therefore the force of attraction acting on a molecule of the surface layer from the side of the molecules of the liquid is greater than that acting from the side of the molecules of the vapour.

Hence it follows that in moving from the surface layer into a liquid a molecule performs *positive* work. Conversely, the transition of molecules from the bulk of a liquid to its surface is attended by *negative* work, i.e. requires the expenditure of external work.

Let us imagine that for some reason or other the surface of a liquid is increased (stretched). This means that a certain number of the molecules pass from the bulk of the liquid into its surface layer. For this purpose, as we have just seen, external work has to be done. In other words, an increase in the surface of a liquid is attended by *negative* work. Conversely, *positive* work is done when the surface is reduced.

If at a constant temperature we reversibly change the surface area of a liquid by an infinitely small amount $dA_s$, the work needed for this is

$$dW = -\sigma\, dA_s \tag{7.20}$$

The minus sign indicates that an increase in the surface area ($dA_s > 0$) is attended by negative work.

The coefficient $\sigma$ is the main quantity characterizing the properties of the surface of a liquid and is called the *coefficient of surface tension*, or simply the *surface tension* ($\sigma > 0$). Consequently, *the surface tension is measured by the work needed to increase the surface area of a liquid at a constant temperature by one unit.*

The surface tension $\sigma$ has the dimension $J/m^2$ in the SI system, and $erg/cm^2$ in the cgs system of units.

It is clear from the above that the molecules of the surface layer of a liquid have a greater (surplus) *potential energy* than the molecules in the bulk of the liquid. Let us denote it by $U_s$. This energy, as always, is measured by the work performed by the molecules of the surface layer while moving into the liquid under the action of the forces of attraction exerted by the molecules in the bulk of the liquid.

Since the energy $U_s$ owes its origin to the presence of a *surface* of a liquid, it must be proportional to the surface area $A_s$ of the liquid:

$$U_s = \sigma A_s \tag{7.21}$$

Hence, a change in the surface area of $dA_s$ will cause a change in the potential energy of

$$dU_s = \sigma \, dA_s$$

which is attended by the work

$$dW = -dU_s = -\sigma \, dA_s$$

in complete accordance with Eq. (7.20).

If, as indicated above, the surface area $A_s$ is changed at a constant temperature, i.e. isothermally (and reversibly), then we know (see Sec. 6.16) that the work needed for this equals the change in the free energy $A$ of the surface:

$$dW = -dA$$

(If the surface area of a liquid is changed adiabatically, its temperature will change. For instance, an increase in the surface area will lead to cooling.) Hence, the surplus potential energy of the surface of a liquid mentioned above is the *free energy* of the surface and, therefore,

$$\sigma = \frac{A}{A_s} \tag{7.22}$$

i.e. the surface tension of a liquid can be defined as the free energy of a unit area of this surface.

It is now clear in what special conditions the surface of a liquid is. These conditions are that the surface of the liquid has a surplus potential (free) energy in comparison with the bulk of the liquid.

Let us see what this leads to.

We know that any system in equilibrium is in that of all the possible states in which its energy is minimum. As applied to the case being considered, this means that a liquid in equilibrium must have the *minimum possible surface area*. This means, in turn, that forces must exist which *prevent an increase in the surface* of a liquid, i.e. which tend to reduce this surface.

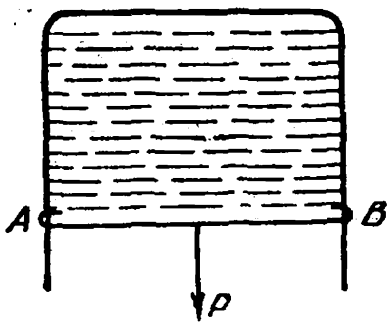


Fig. 107

These forces must obviously be directed along the surface itself, along a *tangent* to it. A liquid behaves as if forces act along a tangent to its surface that contract it. These forces are called *surface tension forces*.

It must be remembered, however, that the original reason for the appearance of surface tension forces are the forces acting on the molecules of the surface layer and directed into the liquid, or in some cases into the neighbouring medium, i.e. at right angles to the surface.

For breaking or dividing a surface, external forces must be applied parallel to the surface and perpendicular to the line along which it is contemplated to divide the surface.

This can be seen especially clearly from experiments with thin films of a liquid. Some liquids such as soapy water and saponin have the property of forming thin films. If, for example, we immerse a wire frame one of whose sides is movable (Fig. 107) into a soap solution, it will become entirely covered with a film of the liquid. The forces of surface tension make the film contract, and movable wire $AB$ moves upward together with the film. To keep it in equilibrium, the force $P$ in the form of a load (including the weight of the movable wire itself) must be applied to the movable wire.

Thus the surface tension force acting in the film is perpendicular to line $AB$, which in the given case is the line of division. The same forces naturally act on the other sides of the frame. But here they are balanced by the forces of attraction of the liquid to the substance of the rigid frame.

The above experiment can be used to determine the numerical value of the surface tension for a liquid forming a film. Indeed, the surface force $f$, taking into account the circumstance that the film has two surfaces (the film is actually a thin layer of liquid), equals in equilibrium the weight $P$ of the load:

$$2f = P \quad \text{and} \quad f = \frac{P}{2}$$

If under the action of this force the movable wire carried along by the film moved over the distance $dh$ from position $AB$, then the work done by the force is

$$dW = f\,dh$$

This work equals the decrease in the free energy of the film which, as we know [see Eq. (7.22)], is $dA = \sigma\, dA_s$. In the given case, the surface area is $dA_s = L\, dh$, where $L$ is the length of the frame. Hence,

$$dW = \sigma L\, dh = f\, dh = \frac{P}{2}\, dh$$

and

$$\sigma = \frac{P}{2L} \tag{7.23}$$

It follows from Eq. (7.23) that the surface tension can be defined as a quantity equal to the *force acting along a tangent to the surface of a liquid per unit length of the line of division.*

The surface tension defined in this way is measured in N/m in the SI system and in dyn/cm in the cgs system of units.

The following simple experiments additionally explain the essence of the forces of surface tension.

A wire ring with a freely suspended (not tensioned) thread attached to it at two points (Fig. 108) is immersed in a soap solution. The ring becomes covered with a thin film of the liquid, and the thread is in equilibrium and arranged randomly. If we now destroy the film at one side of the thread by touching it with a heated needle, then the thread will become stretched and acquire the shape of the arc of a circle. The thread is tensioned under the action of the surface tension force from the side of the contracting film, this force being applied to the thread which in the given case is the line of division. This force is perpendicular to the thread at all points. It had also acted on the thread before the film was destroyed, but identical forces acted on the thread from both sides. After the destruction of one part of the film, the other received the possibility of reducing its area, and the shape of the stretched thread shows that this area became minimum.

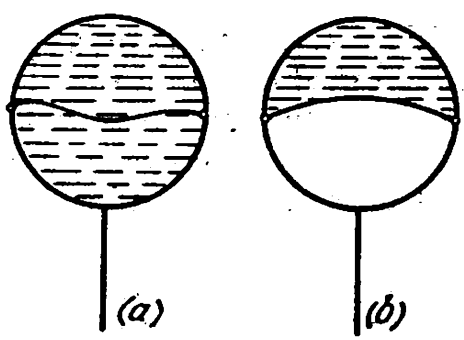



Fig. 108

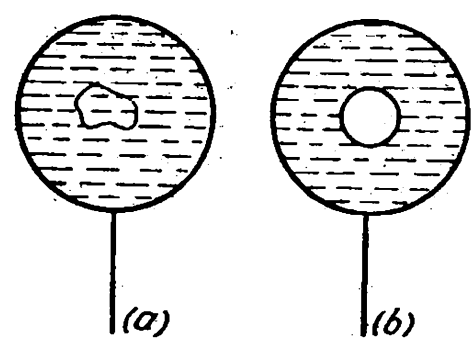



Fig. 109

This experiment can be conducted in the following somewhat altered way (Fig. 109). A loop of a flexible thread is placed on a soap film in the same ring, and the thread acquires a random shape. Let us now destroy

the film inside the loop. The remaining part of the film will contract and stretch out the thread into a circle. This again clearly shows that the surface tension forces are at right angles to the line of division.

The above experiments show that the forces of surface tension appear as a result of a liquid tending to reduce its surface area and, consequently, its surface energy.

Such experiments are conducted with liquids that owing to the specific structure of their molecules easily form thin films. It must be noted that the ability of forming such films is connected not with the value of the surface tension, but with the shape of the molecules. The surface tension of a soap solution, for example, is approximately only one-third of that of pure water, but the latter, however, never forms stable films.

But surface tension manifests itself not only in experiments with thin films. It manifests itself in a whole series of other phenomena, some of which will be treated below.

**The Plateau Experiment.** The tendency of reducing the surface area is naturally characteristic not only of thin films, but also of any volumes of a liquid. And if the surface energy were the only kind of energy determining the behaviour of a liquid, then any mass of a liquid would always have to take on a shape which would ensure that its surface area would be the smallest possible in the given case. Such a shape belongs to a sphere because it is the latter that has the minimum surface area at a given volume.

Apart from the internal forces of interaction between the molecules owing to which the surface tension forces appear, however, external forces also usually act on a liquid. These are, first, the force of gravity, and, second, the forces of interaction of the liquid molecules with particles of the solid walls of the vessel containing it. Hence, the actual shape taken on by a liquid is determined by the relationship between these forces.

Let us first consider the part played by the force of gravity.

This force by itself cannot affect the shape of a liquid because it imparts identical accelerations to all the particles of the liquid.

This explains, for example, why a freely falling liquid takes on a spherical shape. Raindrops are slightly flattened in a vertical direction (like a bread roll) only because of the resistance of the air. For the same reason, a liquid on an artificial satellite takes on the shape of a perfect sphere, as has been described by our cosmonauts. We know that a liquid on an artificial satellite is acted upon only by the force of gravity.

Matters are different when a liquid gets onto a support that is stationary relative to the Earth. In this case, it is acted upon by the upwardly directed force of reaction of the support due to its strain. This force creates a hydrostatic pressure which in a horizontal direction results in spreading out of the liquid.

On an artificial satellite of the Earth, a support is not deformed, and it has no force of reaction.

J. Plateau conducted an experiment in which a liquid having a comparatively great volume took on the shape of a sphere in conditions of equilibrium.

The experiment consists in the following. A certain amount of aniline, which does not dissolve in an aqueous solution of table salt (NaCl), is poured into a vessel containing such a solution (Fig. 110). The concentration of the solution is selected so that its density will equal that of the aniline. The latter will therefore take on the shape of a sphere floating in the solution. The explanation is that the hydrostatic pressure acting from within the liquid aniline is exactly balanced by the external hydrostatic pressure acting from the side of the liquid, and no forces appear that lead to spreading out of the liquid.

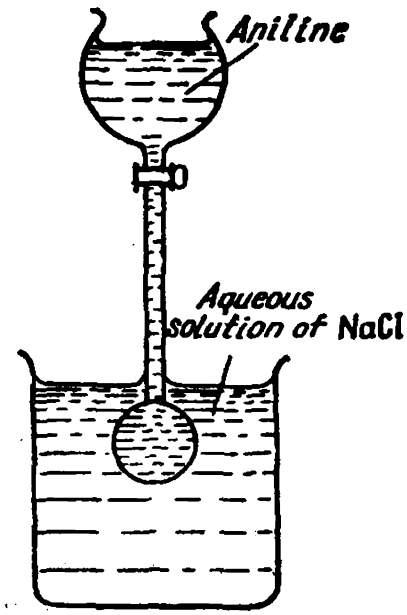


Fig. 110

**Drops of a Liquid.** A liquid acquires a spherical shape not only when the action of the force of gravity is eliminated (as is done, for example, in the Plateau experiment). A small volume of a liquid by itself acquires a shape close to a sphere because owing to the small mass of the liquid the force of gravity acting on it is also small. In this case too, the surface energy exceeds the potential energy of the force of gravity, and the shape of the liquid is determined exactly by this energy.

This explains the spherical shape of small drops of a liquid. Everyone has observed the spherical shape of mercury drops for which the surface tension, as for many other molten metals, is quite high — about 500 dyn/cm. This also explains the almost strictly spherical shape of the drops of a liquid flowing out of a narrow tube.

When the liquid leaves the tube, the size of a drop gradually grows, but it breaks away only after reaching a quite definite size. This occurs because as long as the drop is not big enough, the surface tension forces are sufficient to oppose the force of gravity and prevent separation. The drop will break away when its weight becomes equal to the surface tension force retaining it. Hence, it follows that observation of the breaking away of drops will help us to determine the numerical value of the surface tension.

Figure 111 shows the process of formation of a drop. Before it breaks away, a neck is formed whose radius is somewhat smaller than that of the tube. The surface tension force acts along the circumference of this neck (Fig. 112), and at the moment of separation it should equal the force of gravity.

If the radius of the neck is $r$, and the surface tension is $\sigma$, then the surface tension force obviously equals $2\pi r\sigma$. Consequently, a drop breaks away provided that

$$2\pi r\sigma = P \tag{7.24}$$

By measuring the weight $P$ of a drop that has broken away and the radius of the neck at the moment of separation, we can calculate the surface ten-

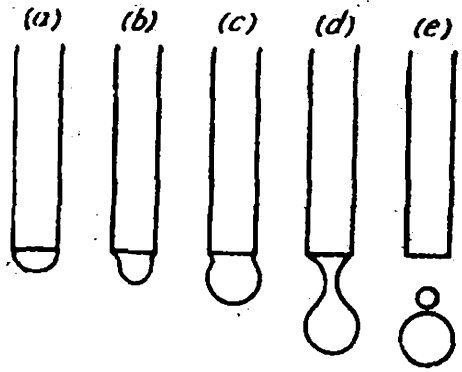



Fig. 111

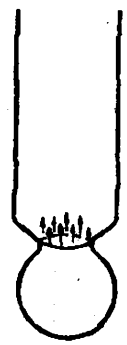


Fig. 112

sion of a liquid. To achieve the required accuracy in determining the radius of the neck, the separating drop is projected with a known enlargement onto a screen, and the diameter is measured on the latter. The weight $P$ of the separated drop is measured on an analytical balance. To increase the accuracy of the measurements, it is customary to gather a definite number of drops and measure their total weight.

The above method of experimental determination of the surface tension gives good results notwithstanding the fact that actually a drop does not break away exactly as described above. It does not separate along the line of the circumference of the neck. At the moment when the size of a drop reaches the value determined by Eq. (7.24), the neck begins to narrow rapidly, as shown in Fig. 111*d*, and is accompanied by another small droplet, as shown in Fig. 111*e*.

**Influence of Second Medium.** It was indicated above that the surface energy of a liquid depends not only on the properties of the liquid itself, but also on the properties of the neighbouring medium. And if we nevertheless introduced the concept of surface tension and related it only to the liquid, we had in mind that the liquid is in contact with its own vapour. The surface energy will remain virtually unchanged, however, if the liquid neighbours with any gas at a low pressure. The explanation is that the interaction of the molecules of the liquid with those of the gas owing to its low density is considerably weaker than the interaction between the molecules of the liquid itself.

Matters are different when a liquid neighbours with another liquid or a solid, or a gas under a great (several hundred atmospheres) pressure. In this case, the densities of the substances are compatible, and we may no

longer ignore the interaction of the liquid molecules with the particles of the medium in contact with it.

Owing to this interaction, the values of the surface tensions of a liquid neighbouring with its own vapour and another denser substance appreciably differ from one another. Hence, in determining the surface tension, it is necessary to take into account the properties of the substances at both sides of the surface.

Table 17 gives data on the surface tension that illustrate this circumstance.

*Table 17*

**Surface Tension for Selected Liquids at Room Temperature**

| Substance | $\sigma \times 10^3$, N/m | Substance | $\sigma \times 10^3$, N/m |
|---|---|---|---|
| Water | 73 | Mercury | 490 |
| Water-benzene | 33.6 | Mercury-water | 427 |
| Water-ether | 12.2 | Mercury-alcohol | 399 |

Inspection of Table 17 shows that the surface tension on the interface between two liquids is always less than for the free surface of a liquid. This is quite natural because the forces of interaction of the molecules of the surface layer with those of the neighbouring medium and with their "own" molecules are directed oppositely.

## 7.5. CONDITIONS OF EQUILIBRIUM ON THE INTERFACE BETWEEN TWO MEDIA CONTACT ANGLE

Let us consider in greater detail the conditions appearing on the interface between two immiscible liquids.

Assume, as is shown in Fig. 113, that a drop of liquid *2* is placed on the surface of another liquid *1* (for example oil on water). The weight of the drop makes it submerge somewhat into liquid *1* forming a lens.

It must be noted, however, that drops of one liquid far from always form a lens on the surface of another one. For instance, petrol and kerosene form not a lens on the surface of water, but a thin film with coloured iridescent

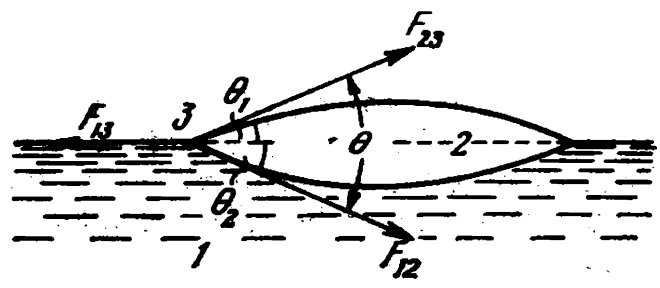



Fig. 113

spots (the latter owe their origin to the phenomenon of interference upon the reflection of sunlight).

Let us see what conditions are needed for a lens to be formed and what for a thin film.

A glance at Fig. 113 shows that in the case under consideration the following media have common interfaces: liquid *1* and liquid *2*; liquids *1* and *2* have a common interface with medium *3*. The latter is a mixture of the vapours of liquids *1* and *2* with air if the experiment is being conducted in air. As we have already indicated, however, the presence of a gaseous medium does not play a significant part.

The circle confining the lens is the interface between the three media. Three surface tension forces act on an element of length $dL$ of this circle:

$F_{12} = \sigma_{12}\, dL$ — the force on the interface between liquids *1* and *2*;

$F_{13} = \sigma_{13}\, dL$ — the force on the "liquid *1*-gas" interface;

$F_{23} = \sigma_{23}\, dL$ — the force on the "liquid *2*-gas" interface.

Each of them is directed along a tangent to the interface between the relevant two media; $\sigma_{12}$, $\sigma_{13}$, and $\sigma_{23}$ are the respective surface tensions (we can consider practically that $\sigma_{13} = \sigma_1$ and $\sigma_{23} = \sigma_2$ because the gaseous medium hardly affects the surface energy of the liquids).

For liquid *2* to be in equilibrium, it is necessary that the sum of the projections of all three forces on the axes of coordinates equal zero (see Fig. 113), i.e.

$$F_{13} = F_{23}\cos\theta_1 + F_{12}\cos\theta_2,\quad 0 = F_{23}\sin\theta_1 - F_{12}\sin\theta_2 \qquad (7.25)$$

or

$$\sigma_{13} = \sigma_{23}\cos\theta_1 + \sigma_{12}\cos\theta_2,\quad 0 = \sigma_{23}\sin\theta_1 - \sigma_{12}\sin\theta_2 \qquad (7.26)$$

Squaring both equations (7.26) and summating them, we get

$$\sigma_{13}^2 = \sigma_{23}^2 + \sigma_{12}^2 + 2\sigma_{23}\sigma_{12}(\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2)$$

or

$$\sigma_{13}^2 = \sigma_{23}^2 + \sigma_{12}^2 + 2\sigma_{23}\sigma_{12}\cos(\theta_1 + \theta_2)$$

Denoting $\theta_1 + \theta_2$ by $\theta$, we have

$$\sigma_{13}^2 = \sigma_{23}^2 + \sigma_{12}^2 + 2\sigma_{23}\sigma_{12}\cos\theta \qquad (7.27)$$

Equations (7.25) or (7.26) and (7.27) determine the angles $\theta_1$, $\theta_2$, and $\theta = \theta_1 + \theta_2$. The angles $\theta_1$ and $\theta_2$, i.e. the angles between tangents to the surfaces of the drop of liquid *2* and the surface of liquid *1* which it is in contact with, are called *contact angles*.

The contact angles (in equilibrium) are determined by the relationship between the three quantities $\sigma_{12}$, $\sigma_{13}$, and $\sigma_{23}$ on the interfaces of the liquids,

i.e. by the relationship between the molecular forces of interaction inside each liquid and between the liquids.

Particularly, the relationship between the quantities $\sigma_{12}$, $\sigma_{13}$, and $\sigma_{23}$ may be such that $\cos\theta = 1$ and, therefore, $\theta = 0$. In this case, liquid *2* spreads out in a thin layer over the surface of liquid *1* (this is how petrol behaves on water). Liquid *1* is said to *completely wet* liquid *2* (or vice versa). Physically, this means that the force $F_{13}$ is greater in magnitude than the resultant of the forces $F_{12} + F_{23}$, i.e.

$$F_{13} \geqslant F_{12} + F_{23} \tag{7.28}$$

It can be seen from Fig. 113 that the resultant force in this case is so directed that it stretches the drop. If $F_{13} < F_{23} + F_{12}$, the liquid will contract until $F_{13}$ becomes equal to $F_{23} + F_{12}$. This is the condition for the formation of a lens:

$$F_{13} = F_{23} + F_{12} \tag{7.29}$$

The well-known unpleasant feeling that appears when castor oil gets into the mouth, although this oil has neither taste nor odour, is explained by the fact that condition (7.28) is observed for it and the saliva. Therefore the castor oil upon coming into contact with the saliva spreads out in a thin layer and fills the entire space of the mouth, also getting into the parotic cavities which foreign substances usually do not get into. This is what causes the unpleasant physiological feeling.

**Interface Between Liquid and Solid.** Similar phenomena occur when a liquid is in contact with a solid. The shape taken by the liquid in this case is determined by the relationship between three forces acting on the liquid: the force of gravity, the forces of interaction of the liquid molecules, and the forces of interaction between the molecules of the liquid and the particles of the solid which it is in contact with. The relationship between the last two forces named is characterized by the contact angle $\theta$, i.e. the angle formed by a tangent to the liquid-solid interface and the surface of the solid.

Suppose that liquid *2* (Fig. 114) is in contact with the flat surface of solid *1*. The magnitude of the contact angle, as in the previous case, is determined from the condition of equilibrium (the sum of the projections of the forces applied to any element of length along the line of contact of the three media *1*, *2*, and *3* must equal zero):

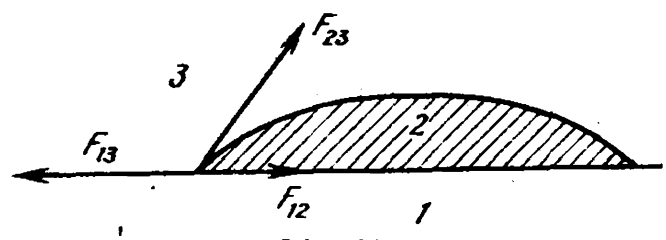


Fig. 114

$$F_{13} = F_{23}\cos\theta + F_{12}$$

whence

$$\cos\theta = \frac{F_{13} - F_{12}}{F_{23}} = \frac{\sigma_{13} - \sigma_{12}}{\sigma_{23}} \tag{7.30}$$

Here $\sigma_{12}$, $\sigma_{13}$, and $\sigma_{23}$ are the corresponding surface tensions, which are also a property of solids. If $\sigma_{13} - \sigma_{12} = \sigma_{23}$, i.e. $\theta = 0$, then the liquid spreads out in a thin layer over the surface of the solid. This will also be observed when $\sigma_{13} - \sigma_{12} > \sigma_{23}$.

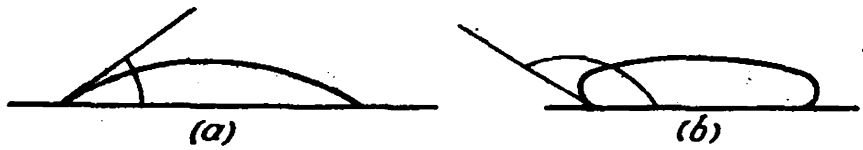



Fig. 115

The phenomenon of complete spreading out of a liquid is called *complete wetting*. It is characteristic, for example, of water on clean glass.

The case $\theta = \pi$ (when $\sigma_{13} + \sigma_{23} = \sigma_{12}$) corresponds to *complete non-wetting* of a solid by a liquid. It is observed, for example, for water on paraffin.

Intermediate cases of *partial wetting* ($\theta < \pi/2$), as shown in Fig. 115*a*, or of *partial non-wetting* ($\theta > \pi/2$), as shown in Fig. 115*b*, are the rule, however.

The interaction of the molecules of a liquid with the particles of a solid also affects the shape of the liquid surface in a vessel. If a large amount of a liquid is pour d into a wide vessel, the shape of its surface is determined by the force of gravity that naturally ensures a flat and horizontal surface (a water table).

At the walls of the vessel, however, the surface of the liquid is nevertheless curved so that a *meniscus* is formed. The latter is concave in wetting liquids (Fig. 116*a*) and convex in non-wetting ones (Fig. 116*b*). The curvature of the surface of a liquid connected with wettability sometimes makes it possible to keep bodies on the surface of a liquid whose density is greater than that of the liquid and which therefore ought to sink in it.

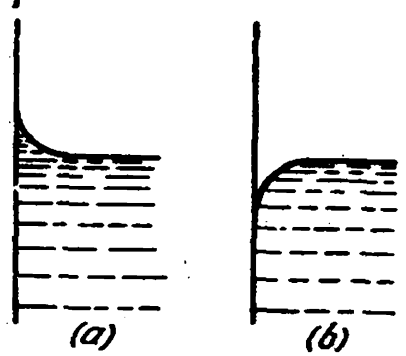



Fig. 116

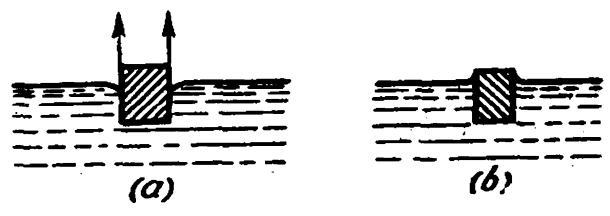



Fig. 117

This peculiar "floating" can easily be explained with the aid of Fig. 117*a* which shows the forces acting on a rectangular bar on the surface of a liquid that does not wet the material of the bar. If the length of the bar in a direction perpendicular to the plane of the drawing is $L$, then the

surface force in the cross section is $2\sigma L$ and is directed upward. This force is balanced by the weight of the bar minus the Archimedean force. When the weight of the bar is sufficiently small, it will remain on the surface. If the material of the bar is wetted by the liquid, then as shown in Fig. 117*b*, the surface tension force may cause the bar to submerge into the liquid even if the density of the bar substance is less than that of the liquid.

## 7.6. FORCES APPEARING ON THE CURVED SURFACE OF A LIQUID

We have seen that the surface of a liquid is often curved. We can even say that a flat surface is not normal for a liquid because the action of an external force — the force of gravity or the force of interaction with particles of the substance neighbouring with the liquid (spreading of the liquid in wetting) — is needed for the surface of a liquid to be flat.

The curvature of the surface of a liquid leads to the appearance of forces acting on the liquid under this surface. This can easily be seen from the following simple considerations. Imagine a spherical drop of a liquid having the radius $r$ (Fig. 118). When the radius of the sphere is increased, the area of its surface also grows, and the surface energy together with it. It is clear that this can be achieved only by doing work. Conversely, when the radius of the drop is diminished, the surface energy decreases. This means that work is done by forces acting in the drop itself. Hence it follows that the volume of a liquid under a spherical surface is always somewhat compressed, i.e. is subjected to an additional pressure directed radially, i.e. at right angles to the surface. These considerations also allow us to calculate the value of this additional pressure connected with curvature of the surface.

Indeed, suppose that the liquid sphere under the action of this pressure reduces its volume by $dV$, as shown in Fig. 118. The work of compression of the liquid is obviously done at the expense of a reduction in the surface energy.* The work of compression $dW$ is known to equal $p\,dV$, where $p$ is the pressure, i.e.

$$dW = p\,dV \tag{7.31}$$

The reduction in the surface energy is

$$dA = \sigma\,dA_s \tag{7.32}$$

where $dA_s$ is the reduction in the surface area of the sphere corresponding to diminishing of the radius by

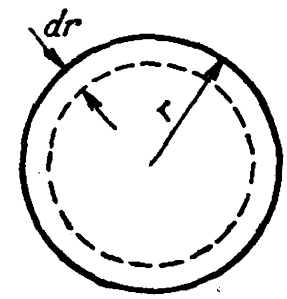


Fig. 118

* The free energy of the liquid, which depends on the volume, also diminishes upon compression. It is compensated by the increase in the free energy of the saturated vapour over the liquid.

$dr$. From the known formulas for the surface area and volume of a sphere $A_s = 4\pi r^2$ and $V = 4\pi r^3/3$, we get the expressions

$$dA_s = 8\pi r\, dr \quad \text{and} \quad dV = 4\pi r^2\, dr$$

Substituting these values for $dA_s$ and $dV$ in Eqs. (7.31) and (7.32) and taking into account that $|dW| = |dA|$, we get

$$p\, 4\pi r^2\, dr = \sigma\, 8\pi r\, dr$$

whence for the pressure exerted on a liquid by its curved surface we get

$$p = \frac{2\sigma}{r} \tag{7.33}$$

If the surface of a liquid is cylindrical instead of spherical, the additional pressure caused by the curvature will be determined by the formula

$$p = \frac{\sigma}{r} \tag{7.34}$$

Indeed, for a cylinder with the length $L$ and the radius $r$, we have $V = \pi r^2 L$, $A_s = 2\pi rL$, and, accordingly,

$$dV = 2\pi Lr\, dr \quad \text{and} \quad dA_s = 2\pi L\, dr$$

whence

$$dW = p\, dV = 2\pi pLr\, dr \quad \text{and} \quad dA = \sigma\, dA_s = 2\pi\sigma L\, dr$$

From the condition that $|dW| = |dA|$, we directly get Eq. (7.34).

In the general case, the pressure due to the curvature of a surface of any shape (not spherical and not cylindrical) is expressed by the *Laplace equation*

$$p = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{7.35}$$

where $r_1$ and $r_2$ are the principal radii of curvature at the given point of the surface or, more precisely, for the given element of the surface.

We can easily see that Eqs. (7.33) and (7.34) are particular cases of Eq. (7.35). In a sphere, both principal radii of curvature coincide and equal the radius of the sphere, i.e. $r_1 = r_2 = r$, and Eq. (7.35) transforms into Eq. (7.33). In a cylinder, one of the principal radii of curvature equals $\infty$, and the other coincides with the radius of the cylinder. Substitution in Eq. (7.35) results in Eq. (7.34).

The additional pressure determined by the Laplace equation is obviously directed toward the centre of curvature of a surface. Hence, with a convex surface, it is directed inside the liquid and is added to the normal pressure of the liquid. With a concave surface, a liquid will be under a pressure that is less than for the same liquid under a flat surface. Mathematically, this

corresponds to the fact that the radius of curvature for a concave surface when the centre of curvature is outside the liquid is considered to be negative and for a convex surface positive.

It must be remembered that the additional pressure created by curvature of the surface and determined by Eq. (7.35) cannot be identified with the surface forces. The latter are directed along a tangent to the surface whereas the additional Laplace pressure is directed at right angles to it. It appears only as a result of the action of surface tension forces that curve the surface of a liquid.

The pressure under the rubber bladder of a ball inflated with air is an analogue of this pressure. The greater the pressure that is naturally directed normally to the surface of the bladder, the more does the envelope of the bladder stretch. But the pressure is directed at right angles to the surface of the bladder whereas the forces stretching its envelope act along a tangent to it (it is only such forces that can stretch the material of the bladder).

The appearance of the additional pressure can be seen especially clearly in Fig. 119 showing part of the spherical surface of a liquid. Surface tension forces directed along a tangent to the surface of the sphere are applied to any element of the length of circle *ABCD*. Inspection of the figure shows that the resultant of these forces is directed toward the centre of the sphere. This resultant force related to a unit surface area is exactly the additional pressure acting on a liquid under a curved surface and expressed by the Laplace equation.

A simple experiment will permit us to easily observe this pressure and watch its qualitative dependence on the radius of curvature. Two ends *A* and *B* of a glass tee (Fig. 120) are lowered into a solution of soapy water. After both of them have been covered with a soap film, the tee is extracted and two soap bubbles are blown through end *C*. As a result of inevitable

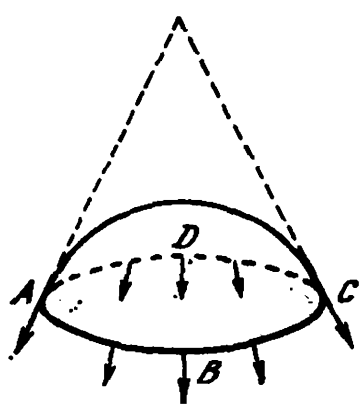



Fig. 119

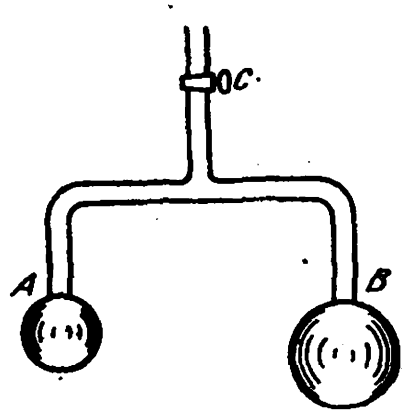



Fig. 120

random circumstances, these bubbles always differ somewhat from each other in diameter. When opening *C* is closed, the bubbles are not in equilibrium. The bubble having the larger radius will expand still more, and

the one having the smaller radius will correspondingly shrink. This shows directly that the pressure caused by curvature of the surface grows with diminishing of the radius of curvature.

## 7.7. CAPILLARY PHENOMENA

We have seen that the surface of a liquid poured into a vessel has a certain curvature near the boundary between the liquid and the solid wall of the vessel, i.e. where the forces of interaction between the molecules of the liquid and solid play an appreciable part. In the remaining part, the surface is flat because the force of gravity suppresses the molecular forces of interaction. If the total area is not great, however, for example when a liquid is in a narrow vessel, the influence of the walls extends to the entire area of the liquid, and it is curved all over its surface (a vessel may be considered narrow when its dimensions are compatible with the radius of curvature of the surface of the liquid in contact with the walls of the vessel).

If the dimensions of the vessel containing a liquid or, in the more general case, if the distance between the surfaces confining a liquid are compatible with the radius of curvature of the surfaces of the liquid, such vessels are called *capillary*. The phenomena in such vessels are called *capillary phenomena*.

Let us consider some of the most characteristic capillary phenomena.

Since capillary vessels (often called simply capillaries) are characterized first of all by the curvature of the surface of the liquid in them, it is quite natural that here the influence of the additional pressure due to curvature of the surface (the Laplace pressure) will be the greatest. A direct result of this additional pressure is the so-called *capillary rise*.

Figure 121 shows a narrow tube immersed in a broad vessel with a liquid. Assume that the walls of the tube are wetted by the liquid. The latter will therefore penetrate into the tube and form a concave meniscus. Assume further that the tube is so narrow that its radius $r$ is compatible with the radius $r_0$ of the meniscus.

Owing to the pressure induced by the curvature of the surface, the liquid filling the tube is acted upon by the pressure $p$ directed toward the centre of curvature of the meniscus, i.e. upward, and equal to $2\sigma/r_0$, where $r_0$ is the radius of the meniscus, and $\sigma$ is the surface tension of the liquid. The liquid rises along the tube under the action of this pressure up to the height $h$ at which the hydrostatic pressure $\rho gh$ of the column of the liquid with the height $h$ balances the pressure $p$. Therefore, the condition of equilibrium will be given by the equation

$$\frac{2\sigma}{r_0} = \rho g h \tag{7.36}$$

where $\rho$ = density of the liquid
$g$ = acceleration of free fall.

This equation determines the height to which a liquid rises in a capillary.

It is not difficult to establish the relationship between the height of rising $h$ and the radius of the tube $r$. We shall turn for this purpose to Fig. 122 in which the meniscus and the capillary are shown to an enlarged scale. The

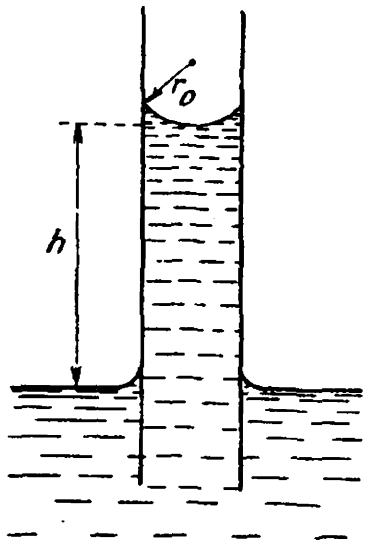



Fig. 121

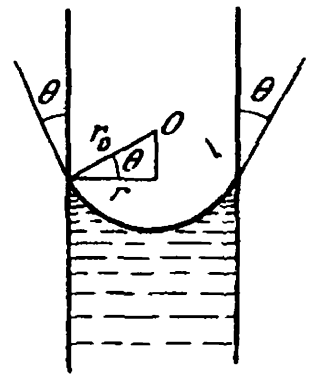



Fig. 122

centre of the sphere which the meniscus is part of is at point $O$. The contact angle between the liquid and the walls of the capillary is $\theta$. It follows directly from the drawing that $r_0 = r/\cos\theta$. Therefore, Eq. (7.36) can be rewritten in the form $2\sigma \cos\theta/r = \rho gh$, whence

$$h = \frac{2\sigma \cos\theta}{\rho g r} \tag{7.37}$$

Particularly, for a liquid that completely wets the walls of the capillary and for which, consequently, $\theta = 0$ and $\cos\theta = 1$, we have

$$h = \frac{2\sigma}{\rho g r} \tag{7.38}$$

As should be expected, the height to which a liquid rises in a capillary (the capillary rise) grows with a decreasing radius of the capillary and with an increasing surface tension of the liquid.

If the liquid does not wet the capillary, we shall have the reverse picture because now the meniscus is convex, the centre of curvature will be inside the liquid instead of outside, and the Laplace pressure will be directed downward. The level of the liquid in the capillary will now be below that in the vessel into which the capillary has been immersed (a negative capillary rise).

Here too, the difference in levels $h$ is determined by Eq. (7.37) or (7.38).

Capillary rise explains a number of well-known phenomena: the absorption of a liquid by filter paper made so that it has narrow winding pores,

the flow of kerosene along a wick whose fibres are also thin capillaries, etc. Capillary forces also ensure the rising of water from the soil along tree runks — the wood fibres play the part of very thin capillaries.

Capillary rise can naturally be observed not only in cylindrical capillaries. A liquid also rises between two plates separated by a narrow gap (Fig. 123). If the plates are parallel to each other, the meniscus has a cylindrical shape. The height of the capillary rise in this case is determined by the equation

$$h = \frac{2\sigma \cos \theta}{\rho g d} \tag{7.39}$$

where $d$ is the distance between the plates. Equation (7.39) is obtained in exactly the same way as Eq. (7.37). It must only be taken into account that a liquid under a *cylindrical surface* is subjected to a pressure equal to $\sigma/R$, where $R$ is the radius of the meniscus (see Fig. 123). It depends on the distance $d$ between the plates as follows:

$$R = \frac{d}{2 \cos \theta} \tag{7.40}$$

Equation (7.39) can be illustrated by the following simple experiment (Fig. 124). Two thoroughly washed glass plates are arranged at an angle to each other so as to form a wedge and are placed in water. The water wets the clean glass and rises, but the height to which it rises in accordance with Eq. (7.39) will diminish with an increasing distance between the plates. This distance grows with an increase in the distance $x$ from the edge of the wedge. If $\varphi$ is the angle between the plates, then the distance between them at small values of $\varphi$ is $d = \varphi x$. Therefore, the height of the level of the liquid $h$ changes with $x$ according to the equation

$$h = \frac{2\sigma \cos \theta}{\rho g \varphi x} = \frac{C}{x} \tag{7.41}$$

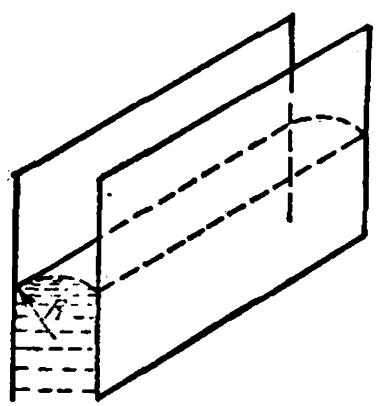


Fig. 123

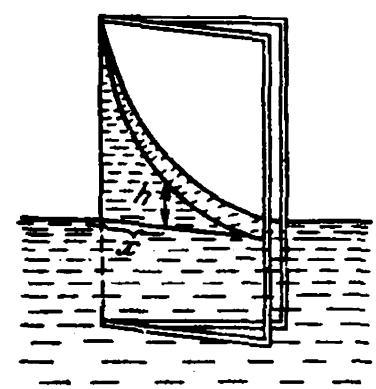



Fig. 124

where $C = \frac{2\sigma \cos \theta}{\rho g \varphi}$ is a constant characteristic of a given pair "solid-liquid" and a given wedge angle. Equation (7.41) is an equation of a hyper-

bola. It is well known that the line of intersection of the surface of a liquid and the plates has exactly such a shape.

The circumstance that the level of the liquid does not extend very high at the edge of the wedge is explained by it being impossible to join the plates very tightly. A small gap always remains between them whose width determines the height of the liquid level at the edge of the wedge, where $x = 0$.

**Forces of Cohesion Between Wetted Plates.** If we place two plates wetted by a liquid together so that the space between them is filled with the liquid, the plates will be pressed against each other (Fig. 125). It is a simple matter

Fig. 125

to calculate the force of attraction between such plates. Any element of the free surface of a liquid owing to wetting is a concave cylinder. The pressure appearing as a result of curvature of the surface will be negative in the given case. Hence, the pressure in the liquid will be less than normal by the quantity $\sigma/r$ [see Eq. (7.34)]. The plates will therefore be subjected to an excess external pressure equal to $\sigma/r$. This excess pressure will press the plates together. The pressure acting on the plates thus equals $\sigma/r$.

A notion of the magnitude of the forces that appear can be obtained from the following numerical example. Let the thickness of the layer of water between glass plates having an area of 10 $cm^2$ be $10^{-4}$ cm (1 micron). The pressure compressing the plates is

$$p = \frac{\sigma}{r} = \frac{7 \times 10^{-2}}{0.5 \times 10^{-6}} = 1.4 \times 10^5 \text{ N/m}^2 \approx 1.38 \text{ atm}$$

(upon complete wetting the radius of the meniscus $r = d/2$, where $d$ is the thickness of the layer of a liquid). At a plate area of 10 $cm^2$ ($10^{-3}$ $m^2$), the force of attraction between them will be

$$f = pA = 1.4 \times 10^5 \times 10^{-3} = 140 \text{ N}$$

Such a force directed at right angles to the plane of the plates must be applied to tear them apart.

But under the action of even a small force applied parallel to the plates they easily slide along each other.

## 7.8. SOME METHODS OF MEASURING THE SURFACE TENSION

Many more accurate methods of determining the surface tension exist in addition to the elementary ones treated above (measurement of the force retaining a thin film of a liquid; the method of separation of drops). Some of them are described below.

**The Method of Capillary Waves.** Capillary waves is another name for the phenomenon of "ripples" on the surface of a liquid that everyone has seen. These waves form under the influence of small disturbances, and their appearance is connected with forces of surface tension. The mechanism of formation of capillary waves can be outlined as follows. Under the action of some external force, the surface of the liquid at a given place is forced inward and becomes concave (Fig. 126*a*). The pressure on the layers of the liquid under this concave surface becomes less (by the magnitude $\sigma/r$) than that in the neighbouring layers where the surface remained flat.

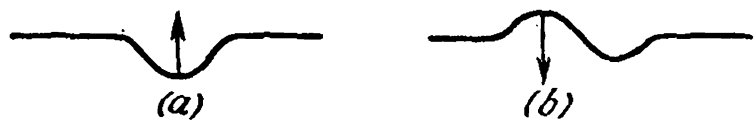



Fig. 126

The resulting pressure difference forces the liquid from the neighbouring layers to flow in under the concave surface, and the liquid again rises to its initial level, but passes it by inertia as a result of the accumulated kinetic energy. The surface therefore becomes convex, and the pressure due to curvature of the surface will now be directed downward (Fig. 126*b*).

It is quite obvious that such oscillations of the liquid at one place will make the adjacent points perform identical oscillations. And this means that the phenomenon has a wave nature. Capillary waves are distinguished by their small amplitude and small wavelength. Owing to the small amplitude, we may ignore the influence of the force of gravity that may exert a similar action (steep ocean waves owe their origin to the force of gravity).

Waves are called capillary only when surface tension forces are the single cause of their formation, and are formed at the expense of a considerable curvature on the crest and in the trough of a wave.

Calculations show that the parameters of capillary waves are related to the surface tension by the following equation:

$$\nu^2\lambda^3\rho = 2\pi\sigma \tag{7.42}$$

where $\nu$ = frequency of the oscillations in a wave

$\lambda$ = wavelength

$\rho$ = density of the liquid.

This equation can be used to determine the surface tension of a liquid whose density is known. For this purpose, we must measure the frequency of the oscillations and the wavelength. Usually the velocity of propagation of the waves is measured, with which the frequency of oscillations is in a simple relationship.

**Drop and Bubble Method.** This method is based on observation of a large drop of a liquid on a flat surface and of an air bubble (also of a large size) in the same liquid.

Assume that a large drop of the liquid being studied has been formed on a horizontal plane (Fig. 127*a*). The drop is so big that its surface is flat all over except for its edges. Assume further that $\theta$ is the contact angle at the boundary of the drop. The drop will be in equilibrium when the absolute values of the forces tending to convert it into a thin film equal the forces

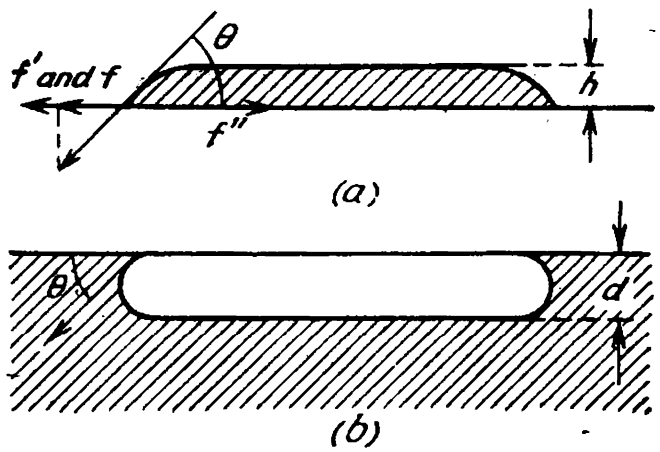



Fig. 127

tending to impart a spherical shape to it. The forces tending to stretch out the drop into a thin film are, first, the force of gravity and, second, the surface tension force at the interface between the liquid and the solid substrate. The surface tension force on the surface of the liquid tends to impart a spherical shape to it.

Let us consider a vertical section of the drop perpendicular to the plane of the drawing and separate in this section an area having the height $h$ (the height of the drop) and a length of 1 cm. A hydrostatic pressure due to the force of gravity acts on this section. Its mean value is $\rho gh/2$, where $\rho$ is the density of the liquid, and $g$ is the acceleration of free fall. The force $f$ due to it equals $(\rho gh/2) \times h = \rho gh^2/2$ (the area of our selected cross section equals $h$!). The direction of this force is shown in Fig. 127*a*.

The horizontal component $f'$ of the surface tension on the interface between the liquid and the substrate related to a unit length equals $\sigma \cos \theta$. Its direction is the same as that of the force $f$, and these two forces tend to convert the drop into a film. These two forces are opposed by the surface tension force $f''$ on the surface of the liquid directed against them and equal to $\sigma$ (per unit length).

Thus, the condition of equilibrium of the drop can be written in the form

$$\sigma = \sigma \cos \theta + \frac{\rho g h^2}{2}$$

or

$$\sigma(1 - \cos \theta) = \rho g \frac{h^2}{2} \qquad (7.43)$$

Let us now consider an air bubble in the same liquid (Fig. 127*b*). If the bubble is big enough for its "bottom" to be flat, then reasoning similar to the above will show that the following equation will express the condition of equilibrium of the bubble:

$$\sigma(1 + \cos\theta) = \rho g \frac{d^2}{2} \tag{7.44}$$

where $d$ is the height of the bubble. Summation of Eqs. (7.43) and (7.44) yields

$$2\sigma = \frac{h^2 + d^2}{2} \rho g \tag{7.45}$$

Hence, to determine the surface tension $\sigma$ of a liquid, it is sufficient to measure the height of the drop and the bubble.

It is interesting to note that the same experiment can be used to find the contact angle $\theta$. Indeed, if we subtract Eq. (7.43) from Eq. (7.44), we get

$$2\sigma \cos\theta = \frac{d^2 - h^2}{2} \rho g$$

Substituting for $2\sigma$ in the latter equation its value from Eq. (7.45) and solving the resulting equation relative to $\cos\theta$, we have

$$\cos\theta = \frac{d^2 - h^2}{d^2 + h^2} \tag{7.46}$$

Consequently, to determine $\theta$ it is also necessary to measure only $d$ and $h$.

Experimentally, the values of $d$ and $h$ are determined with the aid of a manometer having the special shape shown in Fig. 128. After being thoroughly cleaned, the manometer is filled with the liquid being studied, and part of the liquid is then sucked out so as to form a bubble of an adequate size. Next a reading is made on the manometer and this determines the position of the bottom of the bubble. After this, liquid is added to the device so as to form a large drop of the liquid (shown by a dash line in Fig. 128) on the surface of the glass covering the broad limb of the manometer. A new reading on the manometer will give the position of the base of this drop. Finally, a special device (a spherometer) is used to find the height $h$ of the drop. Knowing the thickness of the glass, we can now determine $d$ from the two readings on the manometer and calculate both the surface tension and the contact angle.

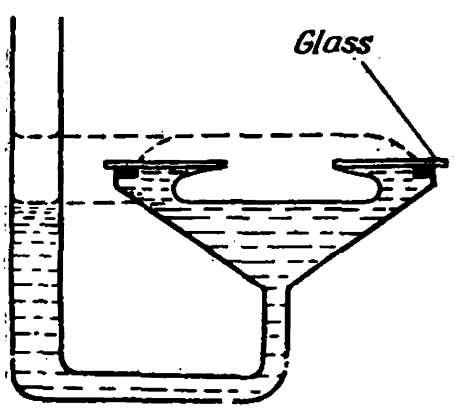


Fig. 128

## 7.9. TEMPERATURE DEPENDENCE OF SURFACE TENSION

It is easy to infer from general considerations that the surface tension should diminish when the temperature rises. This follows from the fact that it must equal zero at the critical temperature because at this temperature the difference between a liquid and its vapour disappears and, consequently, the surface separating the two phases also vanishes. The exact form of the temperature dependence of the surface tension, however, cannot be established theoretically. An approximate equation showing this relationship is

$$\sigma = B(T_{cr} - T - \tau)\left(\frac{\rho}{\mu}\right)^{2/3} \tag{7.47}$$

where $B$ = constant
$T_{cr}$ = critical temperature
$\rho$ = density of the liquid
$\mu$ = molecular weight of the liquid
$\tau$ = small quantity naturally having the dimension of temperature.

Equation (7.47) obviously cannot be applied near the critical point because when $T = T_{cr}$ we should have $\sigma = 0$, but Eq. (7.47) does not give such a result.

It follows from Eq. (7.47) that the temperature dependence of the surface tension, i.e. its change when the temperature changes by one degree, is expressed by the equation

$$\frac{d\sigma}{dT} = -B\left(\frac{\rho}{\mu}\right)^{2/3} \tag{7.48}$$

Examination of this equation shows that the temperature dependence of the surface tension grows with increasing density of a liquid and with decreasing molecular weight of it.

Notwithstanding the approximate nature of Eqs. (7.47) and (7.48), they have so well justified themselves experimentally that they are used for determining the molecular weight of liquids. The constant $B$ is virtually identical for all liquids and equals 2.1 (in the cgs system of units).

## 7.10. EVAPORATION AND BOILING OF LIQUIDS

We saw when considering the van der Waals equation that a liquid can be in equilibrium with its vapour. This equilibrium with the vapour, upon which the latter is called *saturated*, sets in by itself if the liquid is in a closed vessel.

The process of setting in of such equilibrium consists in the following.

Part of the molecules fly out from the surface of the liquid and form a vapour over it. To leave the liquid, the evaporating molecules must overcome the forces of attraction exerted by the remaining molecules, i.e. do work

against these forces. In addition, work must be done against the external pressure $p$ of the already formed vapour equal to $p\Delta V$, where $\Delta V$ is the change in the volume occupied by the given number of molecules upon passing over from the liquid to the vapour (it is clear that the molecules occupy a greater volume when they pass over to the vapour state). All this work can obviously be performed only at the expense of the kinetic energy of thermal motion of the molecules.

It is also clear that not all the molecules are capable of doing this work, but only those of them that have an adequate kinetic energy. Therefore, the transition of part of the molecules to the vapour results in the liquid becoming poorer in rapid molecules, i.e. in its cooling.

If, however, an external source of heat keeps the temperature of the liquid constant, the number of molecules leaving the liquid will continuously grow with time. But together with the transition of the molecules from the bulk of the liquid to the gaseous phase, the reverse process takes place — owing to the chaotic nature of the motion of the vapour molecules part of the molecules that have left the liquid will return to it.

The transition of molecules from a liquid to a vapour is called *vaporization* or *evaporation*. The reverse transition of the molecules from the vapour to the liquid is called *condensation*. It is clear that the number of condensing molecules is proportional to the density of the molecules in the vapour. Therefore, if a vessel is closed, a moment will inevitably set in when the number of molecules leaving the liquid in a unit time becomes equal to the number of molecules returning during the same time to the liquid. In other words, equilibrium will set in, i.e. the amounts of liquid and vapour will become constant.

The constant vapour density that sets in in this way corresponds to a quite definite pressure. The latter, as we already know, is called the *saturated vapour pressure*.

It is not difficult to see that the saturated vapour pressure grows with elevation of the temperature. The higher the temperature, the greater is the number of molecules of a liquid having an energy sufficient for evaporation, and the greater, consequently, must the density of the vapour be for condensation to balance evaporation, i.e. for equilibrium to set in.

An analysis of the van der Waals equation also brought us to the conclusion that the saturated vapour pressure grows with increasing temperature.

**Latent Heat of Vaporization.** The process of evaporation of a liquid, as indicated above, should be attended by its cooling. The feeling of great cooling of the skin wetted with a volatile (i.e. rapidly evaporating) liquid such as ether is a result of this effect. On the other hand, when water poured into a glass evaporates, for instance, we do not note any lowering of its temperature. In such cases, the temperature of the liquid is kept constant at the expense of the heat taken from the surrounding air. Hence, for evaporation of a liquid to be possible without a change in its temperature, heat must be supplied to it.

The quantity of heat that must be supplied for a definite amount of a liquid to evaporate without a change in its temperature (isothermally) at an external pressure equal to its saturated vapour pressure is a characteristic of a liquid and is called the *latent heat of vaporization*. This quantity is usually related to one gramme or to one mole of the liquid. It is called "latent" because the supply of this heat is not attended by any "explicit" effect such as a rise in temperature. The quantity of heat needed for the isothermal vaporization of one mole of a liquid is called the *molar latent heat of vaporization*.

Accordingly, the *specific latent heat of vaporization* is obtained by dividing the molar heat of vaporization by the molecular weight.

The process of condensation that is the reverse of vaporization is attended by the liberation of heat. The latent heat of condensation naturally equals the latent heat of vaporization.

The vaporization of a liquid is one of the kinds of phase transitions. Therefore, the latent heat of vaporization is often called a *heat of transition*. The latent heat of vaporization is obviously a quantitative characteristic of the forces of cohesion between the molecules of a liquid. The greater these forces, the greater is the latent heat of vaporization.

**Measurement of the Latent Heat of Vaporization.** A number of methods are in use for measuring the latent heat of vaporization (or condensation) of a liquid. Most of them are based on the employment of calorimeters to measure the quantity of heat liberated in condensation or absorbed in vaporization. The method of calculating the latent heat of vaporization according to the temperature dependence of the saturated vapour pressure of a liquid will be treated in the following section.

Figure 129 shows an apparatus used for the direct measurement of the latent heat of vaporization of a liquid.

The liquid being studied is poured into vessel $V$ and is heated with the aid of an electric appliance whose winding $W$ is inside the vessel.

As a result of heating, the liquid boils and its vapour enters vertical tube $T$ surrounded by cooling jacket $J$ through which water flows at a constant rate. The direction of flow of the water is indicated in the figure by arrows. The vapour condenses on the water-cooled walls of tube $T$ and flows down through outlet $O$. The latent heat liberated in condensation heats the running water. Therefore, the temperature $t_1$ of the water leaving the jacket is higher than the tempera-

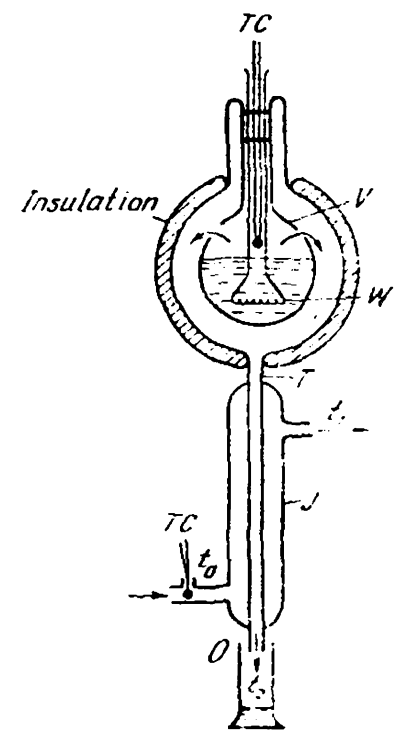


Fig. 129.

ture $t_0$ of the water at its entrance. In addition, the water is also heated as a result of cooling of the already condensed liquid.

To draw up a heat balance of the entire process, it is obviously necessary to measure the following quantities: the temperature $t_0$ of the water entering tube $T$, the temperature $t_1$ of the water leaving the tube (it is also possible to directly measure the difference between these temperatures with the aid of two thermocouples $TC$ connected differentially), the boiling point of the liquid $t_b$, and the temperature $t_2$ of the liquid flowing out through outlet $O$. It is also necessary to measure the mass $m$ of the liquid evaporating in a unit time by weighing the liquid flowing out of $O$ during a definite time, and the mass $M$ of the water flowing through the cooling jacket in a unit time (also by weighing).

The equation of the heat balance obviously has the following form:

$$M(t_1 - t_0) = mL + mc(t_b - t_2) \qquad (7.49)$$

where $L$ = latent heat of vaporization of the liquid being studied
$c$ = its specific heat capacity.

The left-hand side of Eq. (7.49) is the quantity of heat absorbed by the cooling liquid in a unit time. The first term of the right-hand side is the quantity of latent heat liberated in a unit time in condensation of the liquid. The second term of the right-hand side determines the quantity of heat liberated upon cooling of the condensed liquid from its boiling point $t_b$ to the temperature $t_2$ which it had at the outlet from tube $T$.

It is easy to calculate the latent heat of vaporization $L$ from Eq. (7.49).

The apparatus shown in Fig. 129 also makes it possible to determine $L$ in a somewhat different way. Owing to thermal insulation of the vessel, we can consider that all the heat $Q$ liberated by winding $W$ is used only for evaporation of the liquid. And since all the evaporated liquid condenses in tube $T$ and flows out through outlet $O$, we can write

$$Q = mL \qquad (7.50)$$

where $m$ is the mass of the liquid flowing out through $O$. Hence, to determine $L$, we must measure $Q$ and $m$. The quantity of heat can be calculated if we measure the current flowing through winding $W$ and the potential difference across its ends.

The latent heat of vaporization of the majority of liquids is quite great and is therefore measured comparatively easily.

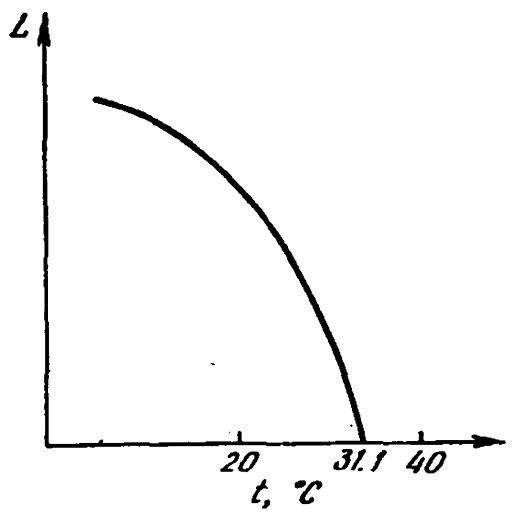


Fig. 130

**Temperature Dependence of Latent Heat of Vaporization.** At the critical temperature $T_{cr}$, when the difference between a vapour and a liquid vanishes, the latent heat of vaporization obviously equals zero. It thus

follows that elevation of the temperature should be attended by diminishing of the latent heat of vaporization. Figure 130 shows an experimentally obtained curve of the temperature dependence of the latent heat of vaporization of carbon dioxide. A glance at the curve shows that the latent heat becomes equal to zero at the critical temperature (31.1 °C).

## 7.11. TEMPERATURE DEPENDENCE OF SATURATED VAPOUR PRESSURE

We already know (for example from our analysis of the van der Waals equation) that the saturated vapour pressure grows quite rapidly with elevation of the temperature. Let us now find the form of this temperature dependence. This can be done approximately by using Boltzmann's law (see Sec. 1.9) according to which the number of molecules $n$ (in a unit volume) having the potential energy $U$ in equilibrium is determined by the equation

$$n = n_0 \exp\left(-\frac{U}{kT}\right) \tag{7.51}$$

where $n_0$ = density (number in a unit volume) of the molecules having a zero energy (relative to the energy $U$)

$T$ = absolute temperature

$k$ = Boltzmann constant.

Equation (7.51) can be applied to the equilibrium of a liquid in contact with its saturated vapour that we are interested in. The molecules departing from the liquid in evaporation do work against the forces of attraction of the other molecules, and their energy changes in comparison with the initial energy by the amount of work done. The mean energy of a molecule that has flown out of the liquid differs from the energy of a molecule inside the liquid by the quantity $L/N_A$, where $L$ is the molar latent heat of vaporization, and $N_A$ is the Avogadro constant. It is exactly the quantity $L/N_A$ (less the work against the external pressure) that is the energy $U$ in Eq. (7.51). Therefore, the density of the vapour molecules $n_v$ is determined by the equation

$$n_v = n_{lq} \exp\left(-\frac{L}{N_A kT}\right) \tag{7.52}$$

where $n_{lq}$ is the density of the molecules of the liquid whose potential energy we assume to equal zero. According to the well-known formula (1.6) of the kinetic theory of gases (see Sec. 1.4), the density of the molecules of a vapour is related to its pressure by the equation

$$n_v = \frac{p}{kT}$$

Using this expression for $n_v$ in Eq. (7.52), we get

$$p = n_v kT = n_{lq} kT \exp\left(-\frac{L}{N_A kT}\right) \tag{7.53}$$

It is exactly this equation that determines the temperature dependence of the saturated vapour pressure. Hence, the saturated vapour pressure grows exponentially with the temperature. Upon strict consideration of Eq. (7.53), we must remember that the quantities $L$ and $n_{lq}$ in it themselves depend on the temperature.

For practical use, it is more convenient to rewrite Eq. (7.53) in the form (remembering that $N_A k = R$)

$$\ln p = -\frac{L}{RT} + \ln T + \ln (kn_{lq})$$

or

$$\ln p = -\frac{L}{RT} + \ln T + C \tag{7.54}$$

where $C = \ln (kn_{lq})$ is a constant characteristic of a given liquid. Since the second term in the right-hand side of Eq. (7.54) is a slowly changing function of the temperature, then in the first approximation it may be considered as a constant quantity and included in the constant $C$. Equation (7.54) therefore becomes

$$\ln p = -\frac{L}{RT} + C \tag{7.55}$$

To graphically depict this function, it is convenient to lay off $1/T$ along the axis of abscissas instead of $T$. The function (7.55) will therefore be shown by a straight line (Fig. 131). The temperature dependence of the saturated vapour pressure has been studied for very many substances, and the results obtained confirm the correctness of Eq. (7.55) and accordingly of the graph in Fig. 131.

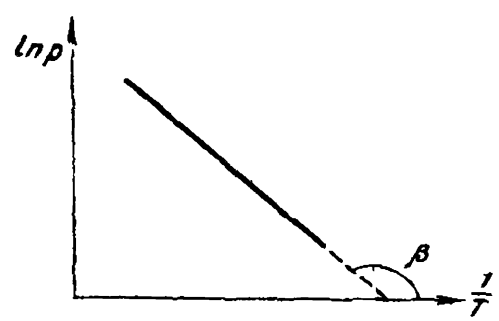


Fig. 131

The slope ($\tan \beta$) of the straight line in Fig. 131 is obviously equal to $L/R$. Consequently, from measurements of the temperature dependence of the saturated vapour pressure of a given substance, we can plot a graph similar to that in Fig. 131 and use it to determine the value of the latent heat of vaporization (molar) for this substance. This is one of the most favoured methods of determining the latent heat of vaporization.

**Thermodynamic Derivation of Temperature Dependence of Saturated Vapour Pressure.** We have seen that Eq. (7.55) has an approximate nature.

An expression similar to Eq. (7.54) can also be obtained in a different way. Let us mentally conduct the following cyclic Carnot process in which the liquid we are interested in is the working substance.

Assume that the initial state is characterized by the temperature $T$ and the pressure $p$, and that the liquid occupies the entire volume of the vessel (there is no vapour phase). The molar volume is $V_1$. This state is graphically depicted by point $A$ on the horizontal portion of the isotherm of a real gas (Fig. 132) corresponding to the temperature $T$ (the molar volume is laid off along the axis of abscissas in Fig. 132). From the experimental viewpoint, this means that our liquid, which is in a vessel provided with a piston (Fig. 133), is in contact with a heat source whose temperature is $T$. The heat of the source causes evaporation of the liquid to begin, and as a result the piston rises — isothermal expansion of the vapour occurs (see Fig. 133*a*). The pressure remains unchanged equal to $p$ (because the vapour is saturated).

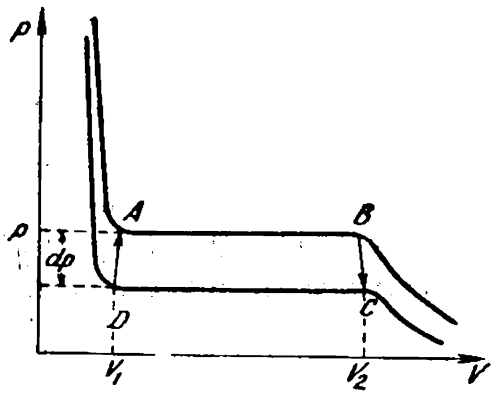


Fig. 132

We shall continue the process until one mole of the liquid evaporates. For this purpose, we have to take an amount of heat $Q_0$ equal to the molar latent heat of vaporization $L$ from the heat source. As a result, the volume of the vapour will grow to the value $V_2$ — the volume occupied by one mole of the vapour at the pressure $p$ and the temperature $T$. Graphically, this corresponds to expansion to point $B$ in Fig. 132. After this, we shall separate the system from the heat source (see Fig. 133*b*) and additionally expand the vapour *adiabatically* so that its temperature will lower by $dT$ and its pressure by $dp$. This part of the cycle is shown by section $BC$ in Fig. 132. Point $C$ depicts the state of the vapour at the pressure $p - dp$ and the temperature $T - dT$.

In this state, we shall bring our system into contact with a heat sink

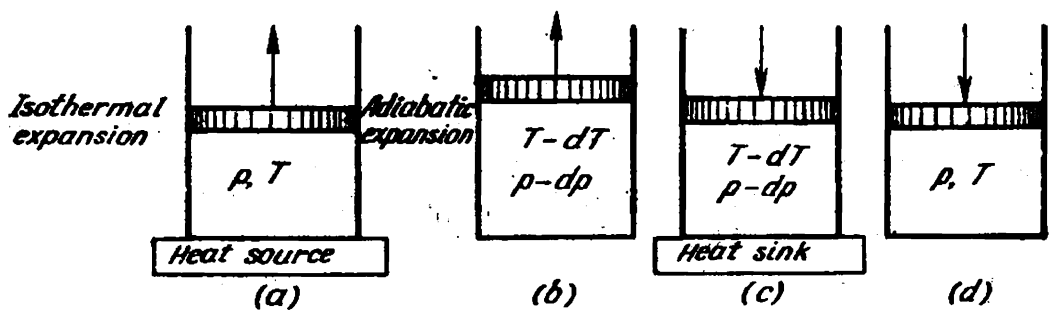


Fig. 133

(see Fig. 133*c*) having the temperature $T - dT$ and perform isothermal compression of the vapour at the constant pressure $p - dp$ up to its complete condensation, i.e. we shall transfer the vapour into the state corres-

ponding to point $D$ along straight line $CD$ of the new isotherm (see Fig. 132) and transfer part of the heat $Q_1$ to the heat sink. Finally, by additional adiabatic compression (see Fig. 133*d*), we shall raise the pressure and the temperature of the vapour to the initial values $p$ and $T$ thus completing a Carnot cycle. The work $dW$ done during the cycle equals area $ABCD$ which may approximately be considered equal to the area of a parallelogram (see Fig. 132):

$$dW = (V_2 - V_1)\, dp$$

The quantity of heat $Q_0$ received from the heat source was shown to equal $L$. Therefore, the efficiency of the above cycle determined by the ratio of the work obtained to the quantity of heat spent (i.e. to the quantity of heat received from the heat source) equals

$$\eta = \frac{V_2 - V_1}{L}\, dp \tag{7.56}$$

On the other hand, the efficiency of a Carnot cycle in all cases is determined by the equation

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{dT}{T} \tag{7.57}$$

Equating the right-hand sides of Eqs. (7.56) and (7.57), we get

$$\frac{V_2 - V_1}{L}\, dp = \frac{dT}{T}$$

or

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \tag{7.58}$$

Equation (7.58) determining the form of the temperature dependence of the saturated vapour pressure is called the *Clapeyron-Clausius equation*. It holds not only for a liquid-vapour transition, but also for all other phase transitions and expresses the change in the pressure at which the phases are in equilibrium when the temperature changes.

Equation (7.58) can be brought into agreement with Eq. (7.55) obtained above. Indeed, $V_2$ and $V_1$ in Eq. (7.58) are the molar volumes of the vapour and the liquid, respectively. If a substance is in a state far from the critical one, the molar volume of the liquid is considerably smaller than that of the vapour (see Sec. 5.2). Hence, the quantity $V_1$ in Eq. (7.58) may be disregarded in comparison with $V_2$. If we also take into account that at comparatively low saturated vapour pressures (far from the critical state) $V_2$ can be expressed through the pressure using the equation of state (1.11), i.e.

$$V_2 = \frac{RT}{p}$$

then Eq. (7.58) can be rewritten in the form

$$\frac{dp}{dT} = \frac{L}{T\frac{RT}{p}} \quad \text{or} \quad \frac{dp}{p} = \frac{L}{R}\frac{dT}{T^2}$$

Integration of the latter equation on the assumption that $L$ is independent of the temperature yields

$$\ln p = -\frac{L}{RT} + C$$

which coincides with Eq. (7.55).

## 7.12. SATURATED VAPOUR PRESSURE OVER CURVED LIQUID SURFACE

Vaporization of a liquid occurs from its surface. Consequently, a change in the properties of the surface layer should change the conditions of equilibrium between a liquid and the vapour over it. Particularly, the curvature of the liquid surface should affect the conditions of equilibrium and, consequently, the saturated vapour pressure. This means that the pressure of a saturated vapour over a curved surface of a liquid should differ from that over a flat surface. We can convince ourselves of the validity of this statement from the most general considerations.

Indeed, when a liquid evaporates from a flat surface, its surface energy does not change because its surface area remains unchanged. But imagine an evaporating *spherical* drop of a liquid. As evaporation proceeds, the radius of the drop and together with it its surface area diminish. Consequently, the surface energy of the liquid in the drop also decreases.

We know that any system tends to pass over to a state of equilibrium in which its energy is minimum (after performing the corresponding work). Therefore, if a closed vessel contains a liquid with a flat surface and a spherical drop of the same liquid, equilibrium will set in only after the drop has completely evaporated and has condensed on the flat surface. This means that the pressure of the saturated vapour over the spherical drop is greater than over the flat surface of the remaining liquid.

This relates not only to a spherical drop, but in general to any liquid with a convex surface. Conversely, the saturated vapour pressure over a concave surface is less than over a flat surface.

It is not difficult to calculate by how much the pressures of a saturated vapour over a curved and a flat surfaces differ from each other.

Imagine a closed vessel (Fig. 134) containing a liquid into which a capillary tube has been partly immersed that is completely wetted by the liquid.

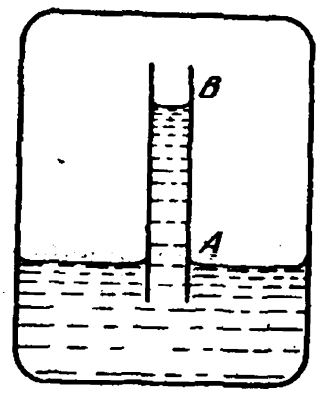


Fig. 134

The capillary forces will cause the liquid to rise in the tube to the height $h$ determined by Eq. (7.38):

$$h = \frac{2\sigma}{\rho g r}$$

where $\sigma$ = surface tension of the liquid
$\rho$ = its density
$r$ = radius of curvature of the concave meniscus in the capillary tube.

Since the vessel is closed, then after equilibrium sets in there will be a *saturated* vapour over the concave surface of the liquid in the capillary tube and over the flat surface in the vessel. But the pressure of the saturated vapour over the concave surface of the liquid in the tube should be less than over the flat surface. Indeed, the pressure $p$ of a saturated vapour at the altitude $h$ (at point $B$) according to the barometric formula [Eq. (1.35), Sec. 1.8] is

$$p = p_0 \exp\left(-\frac{\mu g h}{RT}\right) \tag{7.59}$$

where $p_0$ is the pressure at the surface of the liquid in the vessel (at point $A$).

If the pressure of the saturated vapour over the concave surface in the capillary tube were the same as over the flat surface, it would be greater than the vapour pressure in the surrounding space, and a continuous flow of the vapour from the tube would appear. This is impossible in equilibrium and would transform our apparatus into a perpetual motion machine. Hence, it follows that the pressure of the saturated vapour over the meniscus in the capillary tube should equal $p$ and not $p_0$.

Using the value of $h$ from Eq. (7.38) in Eq. (7.59), we get

$$p = p_0 \exp\left(-\frac{\mu}{\rho RT}\frac{2\sigma}{r}\right)$$

or

$$\ln\frac{p}{p_0} = -\frac{\mu}{\rho RT}\frac{2\sigma}{r} \tag{7.60}$$

The relationship between $p$ and $p_0$, i.e. between the values of the pressure over the curved and the flat surfaces of the liquid (naturally at the same temperature) can be written in a more convenient, though approximate form holding only at small values of $p - p_0$, namely when $|p - p_0| \ll p_0$. The difference between the pressures of the vapour at points $A$ and $B$ can approximately be considered equal to the pressure of a column of saturated vapour having the height $h$:

$$p_A - p_B = p_0 - p = \rho_0 g h$$

where $\rho_0$ is the density of the saturated vapour. But $h = 2\sigma/\rho gr$ so that

$$p = p_0 - \frac{2\sigma}{r}\frac{\rho_0}{\rho} \tag{7.61}$$

We thus see that the pressure of the saturated vapour over a concave surface is less than over a flat one by the quantity $(2\sigma/r)(\rho_0/\rho)$.

It is clear that we can show in exactly the same way, by placing a capillary tube in a non-wetting liquid, that the pressure of the saturated vapour of a liquid is greater over a convex surface of a liquid than over a flat one by the same quantity $(2\sigma/r)(\rho_0/\rho)$.

The difference between the values of the saturated vapour pressures over a flat and a curved surfaces is connected exclusively with the curvature of the surface. Neither the force of gravity nor the difference in heights plays any part here. This can already be seen from the fact that Eqs. (7.60) and (7.61) include neither the acceleration of free fall $g$ nor the height $h$, but do include the radius of curvature of the surface $r$. These equations therefore relate not only to the case when the surface of a liquid is curved because it is in a capillary, but also to such cases as a drop of a liquid (a convex surface) or a gas bubble in a liquid (a concave surface).

We shall give an example showing the influence of the curvature of a liquid surface.

Let us consider the condition of equilibrium of a spherical drop of water and its saturated vapour at an ambient temperature of 27 °C (300 K). At this temperature, we have $\sigma = 7.3 \times 10^{-2}$ N/m (73 dyn/cm). The density $\rho$ of water is 1000 kg/m$^3$ (1 g/cm$^3$), and its mass is $\mu = 18 \times 10^{-3}$ kg/mol. Hence, by Eq. (7.60) we find

$$\ln\frac{p}{p_0} = \frac{2 \times 7.3 \times 10^{-2} \times 18 \times 10^{-3}}{8.31 \times 300\, r} = \frac{1.05 \times 10^{-7}}{r}$$

When the radius of a drop is, for instance, $10^{-5}$ m (fog drops), we have $p/p_0 = 1.01$, i.e. the saturated vapour pressure differs by only one per cent from the normal value (for a flat surface). But already when the radius of a drop $r = 10^{-9}$ m, we have $p/p_0 = 3$, i.e. the vapour pressure is three times greater than the normal value.

This circumstance plays an appreciable part in such phenomena as the formation of raindrops and the boiling of a liquid.

Indeed, such conditions are often created in the atmosphere in which the partial pressure of water vapour exceeds the saturated vapour pressure at the same temperature. For equilibrium to set in, the vapour must condense and form drops of the liquid. This occurs, however, far from always. At the very beginning of the condensation process, the drops are naturally very small in size. And this means that the pressure of the vapour over them is much greater than normal. It is also greater than the partial

pressure of the water vapour in the atmosphere. The drops therefore evaporate before they reach a size sufficient for rainfall. Growth of the drops formed is possible if the partial pressure of the water vapour in the air is greater not only than the saturated vapour pressure at the same temperature, but also than the vapour pressure over the surface of a drop having a small radius. Otherwise for the drops to grow, they must have a sufficiently great size from the very beginning.

This explains why the presence in the atmosphere of tiny dust particles (aerosols) noticeably facilitates the condensation of vapour and the formation of sufficiently large drops which then precipitate in the form of rain. The dust particles on which condensation of the water vapour begins ensure a considerable radius of the drops forming on them from the very beginning. The vapour pressure over them is only slightly greater than that over a flat surface. In these conditions, even a slight supersaturation of the air with moisture is enough for the drops to be able to form and grow without hindrance until they form rainfall.

Dust particles thus serve as centres of condensation of the vapour. It is quite obvious that a supersaturated vapour, i.e. a vapour whose pressure exceeds that of a saturated vapour, can exist only if centres of condensation are absent. The existence of such embryos (centres) is an essential condition for vapour condensation. It is sometimes even possible to cause rainfall by artificially introducing dust particles into the atmosphere for forming condensation centres. True, a high dust content in the air more often results in the formation of dense fogs than of rain.

Experiments show that in addition to dust particles, electrically charged particles, particularly ionized atoms present in a gas, can be centres of condensation.

**Wilson Cloud Chamber.** This is a wonderful device based on the phenomenon of the formation of drops on ionized atoms and having an exceedingly great significance in nuclear research. It is a vessel divided by a piston or an elastic, for instance rubber, membrane into two parts not communicating with each other (Fig. 135). The space over the piston is filled with a gas containing saturated vapour of a liquid — generally argon and a mixture of alcohol and water vapours. If the piston or membrane is rapidly lowered in some way or other, the mixture filling the chamber will rapidly (adiabatically) expand and cool. The vapour will become supersaturated, but there will be no condensation because special procedures are used to ensure the absence of centres of condensation in the chamber. But if during this expansion a fast particle flies through the chamber that is capable of ionizing the atoms (molecules) in it, a train of ions will appear along its path. These ions will serve as embryos or seeds on which condensation of the vapour and the formation of drops of a fog will begin. If the working space of the chamber is adequately illuminated, the train of drops along the path of the particle becomes visible and can be photographed.

This is one way of observing and studying the particles of cosmic rays and nuclear particles.

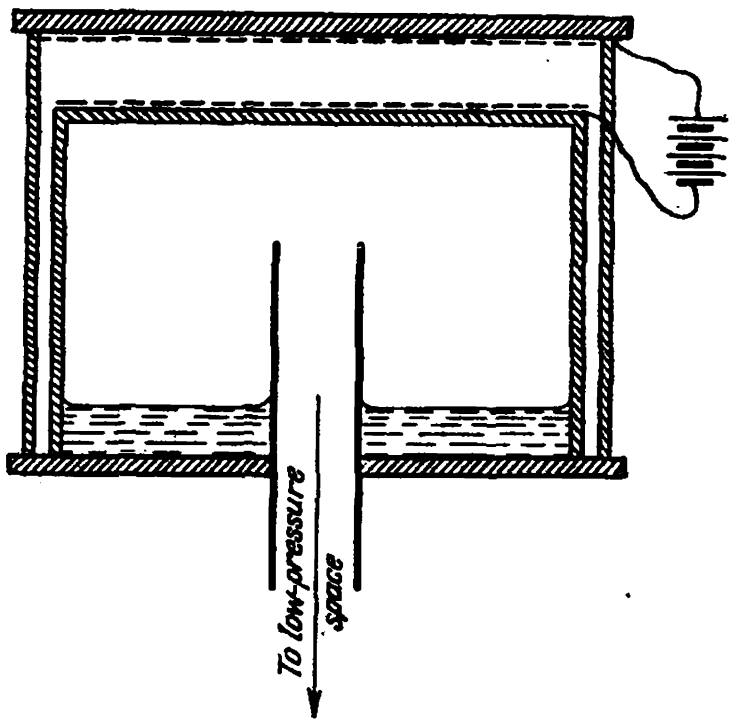



Fig. 135

## 7.13. BOILING OF LIQUIDS

It is general knowledge that every substance boils at definite values of the temperature and external pressure.

By *boiling* is meant the process of vaporization of a liquid attended by the rapid formation and growth of vapour bubbles that break outward through the surface of the liquid.

Let us consider the conditions in which boiling occurs.

A bubble of vapour may form in a liquid if a region having a reduced density appears somewhere in the liquid. In principle, such a region can appear because owing to the chaotic nature of thermal movements chance deviations from the mean uniform distribution of the particles in the volume occupied by the liquid are not only possible, but are even inevitable. Such deviations from the mean value, as indicated on a previous page, are called fluctuations. Such fluctuations result in bubbles of vapour in a liquid. But here the following must be borne in mind.

The density of a vapour at a temperature far from the critical one is thousands of times smaller than that of the liquid. Consequently, for a bubble to form, a quite considerable fluctuation is needed: a region must be formed by chance in which the density is thousands of times smaller than in the remaining volume of the liquid! The probability of such a fluc-

tuation is therefore very low. The probability that it will cover a more or less considerable volume is still smaller. In the overwhelming majority of cases, the bubbles, if they do form, are very small in size. But in this case, they do not have the proper conditions for growth. We can say that a bubble is a vessel containing a saturated vapour (because the vessel is closed), and the concave surface of the liquid around the bubble forms the walls of the vessel. Owing to curvature of the surface, a force appears that is directed toward the centre of curvature. This force will crush the bubble because it is very great when the size of the bubble is small.

It would seem that in such conditions no vapour bubbles could really form in a liquid and, therefore, boiling is impossible. Matters appreciably change, however, if the liquid itself or the walls of the vessel confining it contain dissolved or absorbed (adsorbed) air (or some other gas). In this case, bubbles of the gas will form in the liquid when it is heated, and their formation is not connected with fluctuations of the density of the liquid. Therefore, they may not be too small from the very beginning, and the pressure connected with curvature of the surface must not necessarily crush them.

Gas bubbles thus play the same part in the phenomenon of vaporization (boiling) as dust particles or ions do in the phenomenon of condensation, i.e. the part of embryos or seeds.

Thus, let us assume that a gas bubble has formed in a liquid for some reason or other. After its formation, it will immediately be filled with the saturated vapour of the surrounding liquid and will be in equilibrium with it. The vapour pressure inside the bubble will be determined by the temperature of the liquid. As long as the temperature of the liquid is such that the pressure of the saturated vapour inside a bubble is lower than the external pressure over the liquid, the bubble cannot grow because now too there is no lack of forces tending to crush it. As previously, there is the force connected with the curvature of the surface of the liquid surrounding the bubble. In addition, the bubble is acted upon by the hydrostatic pressure of the column of the liquid over it. Finally, the bubble is acted upon by the external pressure under which the entire liquid is, and it is exactly this pressure that plays the main part. The other two forces only facilitate crushing of the bubble by the external pressure.

But when the temperature of the liquid reaches a value at which the pressure of its saturated vapour will become equal to the external pressure, the pressure of the vapour inside a bubble will also be equal to the external pressure (if we meanwhile ignore the hydrostatic pressure and the pressure due to curvature of the surface). Now a very negligible increase in the temperature will be sufficient for the vapour pressure inside the bubble to exceed the external pressure. Under the action of this pressure difference, the bubble will rapidly begin to swell, and it will finally rise to the surface and break through it.

Hence, a liquid in boiling evaporates not only from its surface, but also from the surface of the bubbles inside the liquid. For the liquid to boil,

its temperature must be raised to the value at which the saturated vapour pressure of the liquid equals the external pressure (to be more exact, it must be somewhat greater).

It is clear that the lower the external pressure, the lower is the boiling point of a liquid. This explains the well-known fact that at high altitudes, where the atmospheric pressure is reduced, liquids boil at temperatures that are lower than at sea level. By measuring the boiling point of a liquid, we can determine the barometric pressure and, consequently, the altitude above sea level. The corresponding instrument is called a *hypsothermometer.*

Water, which normally (i.e. at an external pressure of 1 atm) boils at 100 °C (it is exactly at this temperature that the saturated vapour pressure of water equals 1 atm), can also boil at room temperature if we reduce the external pressure over it by the intensive evacuation of the air and vapour over its surface.

It is easy to establish the form of the dependence of the boiling point of a liquid on the external pressure. Indeed, above we obtained Eq. (7.58) determining the temperature dependence of the saturated vapour pressure of a liquid, namely,

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$

(the Clapeyron-Clausius equation). Since in boiling the external pressure exactly equals the saturated vapour pressure of a liquid, it is quite clear that if we invert the Clapeyron-Clausius equation, we shall get the dependence of the boiling point of the liquid on the external pressure. Consequently, this relationship has the form

$$\frac{dT}{dp} = \frac{T(V_2 - V_1)}{L} \tag{7.62}$$

**Superheating of a Liquid.** It is clear from what has been said above that the phenomenon of boiling can occur only if gas bubbles can form in a liquid, and for this to happen the liquid must contain dissolved gases. We can say that just like condensation is possible only when centres of condensation are present (dust particles, ions), boiling, i.e. intensive vaporization, requires the presence of centres of vaporization, and gas bubbles are such centres. (Phase transitions occurring only upon the presence of embryos or seeds are called *phase transitions of the first kind* or *first-order transitions.*)

In the absence of centres of condensation, we can obtain, as we have already seen, a supersaturated vapour. In exactly the same way when dissolved gases that can form bubbles are absent in a liquid, we can obtain a *superheated liquid*, i.e. a liquid whose temperature is higher than the boiling point at a given external pressure, but which nevertheless does not boil.

The possibility of superheating of a liquid is connected with the additional pressure acting on the liquid under a curved surface. Indeed, the spherical surface of a liquid surrounding a bubble tends to contract. The pressure $\Delta p = 2\sigma/r$ appearing as a result of this is directed toward the centre of the bubble, i.e. is added to the external pressure crushing the bubble. And when a bubble has a small size, the value of $\Delta p$ is quite great. Consequently, if the liquid being heated and the walls of the vessel containing it are thoroughly cleaned of the dissolved gases, then it will be so difficult for bubbles to form in the liquid that it can be heated without its boiling to a temperature considerably higher than the boiling point. More exactly, the liquid can be heated to such a temperature at which the pressure of the saturated vapour in the bubbles does not exceed the external pressure plus the pressure due to the curvature of the surface of the smallest bubbles.

We have seen that the formation of vapour bubbles at low temperatures is virtually impossible owing to the fact that this requires great fluctuations of the density whose probability is very small. But with elevation of the temperature, the difference between the densities of the liquid and the vapour diminishes (it completely vanishes at the critical temperature). Hence the fluctuations of the density needed for the formation of bubbles become less and less considerable. Their probability grows correspondingly. At a sufficiently high temperature (here high means close to the critical value), bubbles may form and grow even in the absence of seeds in the form of gas bubbles. Hence, in this case too, boiling of the liquid is possible, but only when it has been superheated. And the more thoroughly the liquid has been purified, the more can it be superheated.

When a superheated liquid nevertheless finally does boil, the boiling is very violent and reminds one of an explosion. The liquid rapidly cools to the normal boiling point at the given pressure.

Superheating of a liquid and the following violent boiling are very dangerous for the vessel containing the liquid. Special measures are therefore taken to prevent superheating. For this purpose, porous bodies are placed in the liquid, and an abundant amount of air is liberated from them upon heating. Such bodies include ceramic tubes (for instance unbaked porcelain) and lengths of capillary tubes.

It is not difficult to determine the size of bubbles that will prevent appreciable overheating of a liquid. Let us do this for water. We shall consider here that superheating of water by 0.1 kelvin is permissible at a normal external pressure.

What should the dimensions of the bubbles be for superheating not to exceed this value?

For this purpose, we must determine by how much the vapour pressure will grow when the temperature rises from 100 to 100.1 °C. This can be done by using a curve of the temperature dependence of the vapour pressure of water. We can determine from this curve that a change in temperature by 0.1 K causes the vapour pressure to change by about $3 \times 10^{-3}$ atm

or about $3 \times 10^3$ dyn/cm$^2$. Hence, for superheating not to exceed 0.1 kelvin, the mean radius of the bubbles should be at least

$$r = \frac{2\sigma}{\Delta p} \approx \frac{2 \times 70}{3 \times 10^3} \approx 0.5 \text{ mm}$$

Let us also assess the influence of the hydrostatic pressure acting on the bubbles on superheating of a liquid.

At the depth $h$ under the surface of a liquid, a gas bubble is acted upon by the pressure

$$\Delta p' = \rho g h$$

It is added to the external pressure (like the pressure due to the curvature of the surface of a bubble), and the vapour pressure inside the bubble must increase by this value for the bubble to rise to the surface. We can find from the same curve by how much the temperature of water in boiling changes with a change in the depth under the surface. At $h = 1$ cm, for instance, we have

$$\Delta p' = 1 \times 1 \times 981 \approx 10^3 \text{ dyn/cm}^2 \approx 10^{-3} \text{ atm}$$

This corresponds to elevation of the boiling point by 0.03 K.

We see that the temperature of boiling water is not an entirely definite quantity. For reasons which we have just considered, it fluctuates within small limits. It is not the boiling water itself that has a quite definite temperature, but the vapour (or steam in the case of water) above it because no matter what happens inside a liquid the vapour emerging from the bubbles bursting at its surface has a quite definite temperature — the temperature at which the saturated vapour pressure equals the external pressure. This is why thermometers when being graduated are placed into the steam over boiling water instead of into the water itself.

**Bubble Chamber.** We have seen that a Wilson cloud chamber uses the supersaturation of vapour and the condensation of the supersaturated vapour on ions as centres of condensation. The phenomenon of superheating of a liquid with the following formation of bubbles in it can be used in a similar way and for the same purposes, i.e. for registering fast particles. The functioning of the so-called *bubble chamber* is based on this principle. It has lately come into great favour in research in the field of nuclear physics and the physics of high-energy particles.

A bubble chamber is a vessel containing a liquid that can be superheated by means of a heater. The vessel is connected to a device that makes it possible to create an increased pressure over a liquid and to rapidly diminish this pressure. If we first heat a liquid and compress it by applying an external pressure, and then lower the external pressure, the liquid will naturally be superheated. During the time sufficient for an experiment (several scores of seconds), however, it does not boil. If a fast particle

flies into the chamber, it will lose part of its energy along its path in the liquid, and this energy will mainly be transformed into heat. Since the liquid is superheated, this additional heat is sufficient for the intensive formation of bubbles along the path of a particle. The bubbles formed will rapidly grow to a size at which they become visible so that the train of bubbles — the trace of the particle — can be photographed.

Whereas a particle can fly completely through a Wilson cloud chamber filled with a vapour having a low density, in a bubble chamber filled with a dense substance — a liquid — a particle will complete its path without leaving the chamber. This makes it easier to study the properties of this particle. This is one of the important advantages of a bubble chamber.

## 7.14. LIQUID SOLUTIONS

We comparatively rarely have to do with pure liquids, i.e. liquids containing particles of a single species. The liquids generally encountered are a mixture of different substances. If one of these substances is contained in such a mixture in a much greater amount than the others, the mixture is alled a *solution*, and the predominating substance is called a *solvent*. In this section, we shall acquaint ourselves with some properties of *liquid* solutions. We shall limit ourselves to binary solutions consisting of only two substances — a *solvent* and a *solute* (the dissolved substance).

**Concentration.** Solutions are quantitatively characterized by their *concentration* determining the content of the solvent and the solute. The concentration can be expressed in many ways. We shall consider only the most important ones here.

1. *Mass fraction* — the ratio of the mass of a given component to the mass of the entire solution. If it is expressed in per cent, we have the *mass concentration.*

2. *Mole fraction* — the ratio of the number of moles of a solute to the total number of moles in a solution. If it is expressed in per cent, we have the *molar concentration.* This way of setting the concentration is especially convenient because at the same time it determines the ratio of the number of molecules forming a solution of substances. The *atomic concentration* is determined in exactly the same way for substances consisting of atoms instead of molecules. If a solution contains $n_1$ moles of one substance and $n_2$ moles of the second one, then the mole fractions of the first and second substances are expressed as follows:

$$x_1 = \frac{n_1}{n_1 + n_2} \quad \text{and} \quad x_2 = \frac{n_2}{n_1 + n_2}$$

3. *Molality* — the number of moles of a solute in 1000 grammes of the solvent.

It is naturally quite simple to convert the different values of the concentrations obtained in this way into one another.

In some special cases, the concentration of a solution is characterized by the magnitude of its density and is expressed in special arbitrary units: in graduations of an instrument used to measure density — an *areometer*. When studying the properties of solutions, the concentration, in addition to the pressure and temperature, is a basic parameter of state.

Sometimes substances can dissolve in each other in an unlimited amount, i.e. the solution can be of any concentration. An example is a solution of alcohol in water or of water in alcohol. There are also such substances, however, that can dissolve in a given solvent only up to a definite maximum concentration. Further dissolving at the given temperature and pressure is impossible. This maximum equilibrium concentration is called the *solubility*. A solution with the maximum concentration (i.e. with a concentration equal to the solubility) is called a *saturated solution*. The solubility usually depends on the temperature and the pressure and, generally speaking, grows with increasing temperature and diminishes with increasing pressure.

**Mechanism of Dissolution.** Many properties of solutions even at low concentrations of the solute appreciably differ from those of the pure liquids, particularly from those of the pure solvent. This is connected with the fact that in solutions we have to do with more complicated interactions of the particles. If the properties of conventional liquids are determined by the interactions between the particles, this also holds for solutions.

But in pure liquids, all the particles are identical whereas particles of different substances are present in solutions. If, for instance, substance *B* is dissolved in liquid *A*, then of significance in such a solution are the interactions of particles of *A* with one another (the interactions *A-A*), of particles of *B* with one another (the interactions *B-B*), and of particles of *A* with particles of *B* (the interactions *A-B*). All these interactions are different. The magnitude and the relative part of each of them depend on the concentration, and it is therefore clear that a liquid solution is a considerably more complicated system than a conventional liquid, although the solute is *uniformly* distributed in the solvent so that a *solution is a single-phase system*.

Dissolution itself is the result of interaction of solute particles with solvent particles. The latter weaken the forces of attraction holding the solute particles together so that owing to thermal motion they move apart and gradually (by a diffusion mechanism) become distributed over the entire volume of the solvent. In many cases, dissolution is attended by a change in the very nature of the solute particles. This occurs, for example, when salts, acids, and alkalies are dissolved in water. The molecules of such substances in a solution decompose into separate parts — ions, carrying a positive or a negative charge so that the solution no longer contains the molecules which the substance had been made of before it dissolved.

**Heat of Solution.** The separation of the solute particles and their transfer into the solution requires the expenditure of energy. We know that these

particles before dissolving are connected to one another by forces of attraction, and work must be done against these forces. This work is done by the forces of interaction between the particles of the solute and the solvent. The energy spent for dissolving is called the *heat of solution.* It is related to one mole of the solute and is measured in *joules per mole.*

Since the heat used for dissolution (separation of the solute particles) is taken from the store of internal energy of the solvent, then dissolution should result in cooling of the solvent and, therefore, of the entire solution. This is exactly how matters are in many cases, for instance when salts are dissolved in water. Dissolving, however, often results not in cooling, but, on the contrary, in heating of the solution. Everyone knows, for example, the great heating of the liquid that attends the dissolving of sulphuric acid in water. The explanation is that especially great forces of attraction may act between the particles of the solvent and the solute, owing to which they may rush toward one another with great velocities and combine into special complexes. The heat liberated as a result of this not only compensates for, but is even considerably greater than the cooling effect in dissolution.

Such solutions are also conceivable upon whose formation heat is neither liberated nor absorbed. For this to happen, the forces of interaction between any particles in the solution must be the same. This means that all three kinds of interaction (*A-A*, *B-B*, and *A-B*) must be identical. Such solutions are called *ideal.* Some real solutions such as methyl alcohol ($CH_3OH$) in ethyl alcohol ($C_2H_5OH$), and benzene in toluene are close to them. According to some features, any real solutions may be considered to be ideal if the concentration of the solute in them is sufficiently small.

**Saturated Vapour Pressure over an Ideal Solution.** Owing to the presence of the solute, the number of molecules of the solvent on the surface of the latter (and also in the bulk of it) is less than it would be in the pure solvent. Accordingly, the number of solvent molecules evaporating from such a surface and, consequently, the pressure of its saturated vapour over the solution will be less than over the surface of the pure substance (if the solute can also evaporate, then we are speaking here of the partial pressure of the solvent vapour).

It is not difficult to see that this vapour pressure should be proportional to the concentration of the solvent in the solution. If solute $B$ is dissolved in solvent $A$, and the concentration of $A$ is $x_A$, then the vapour pressure $p_A$ is determined by the obvious equation

$$p_A = x_A p_A^\circ = \frac{n_A}{n_A + n_B} p_A^\circ \tag{7.63}$$

where $n_A$ and $n_B$ = numbers of moles of substances $A$ and $B$, respectively
$p_A^\circ$ = saturated vapour pressure of the pure substance $A$ at the same temperature (the superscript "°" stands for a pure substance).

The same reasoning naturally relates to the solute, for which a similar equation holds:

$$p_B = x_B p_B^\circ = \frac{n_B}{n_A + n_B} p_B^\circ \tag{7.64}$$

where $p_B^\circ$ is the saturated vapour pressure over the pure substance *B*.

The simple law expressed by Eqs. (7.63) and (7.64) is called *Raoult's law* (1884). We have already indicated that this law is true for ideal solutions. It is also obeyed quite well, however, for any *weak* or *dilute* solutions. But in the latter case we are usually speaking about the vapour pressure of the solvent (it was exactly for this case that F. Raoult discovered the law bearing his name). In the particular case when a non-volatile substance is dissolved in a liquid solvent, the vapour over the solution consists exclusively of solvent particles.

It is not difficult to note that Eqs. (7.63) and (7.64) can also be written in the following form:

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A + n_B} \quad \text{and} \quad \frac{p_B^\circ - p_B}{p_B^\circ} = \frac{n_A}{n_A + n_B} \tag{7.65}$$

The left-hand sides of these equations contain the relative change in the vapour pressure of one of the components as a result of the fact that it enters the composition of the solution. Examination of the equations shows that the relative change in the equilibrium vapour pressure of one of the components equals the concentration of the other component. Particularly, when the solute is not volatile, the first of the two equations (7.65) means that the relative change in the saturated vapour pressure of the solvent equals the concentration of the solute.

In real solutions, the change in the vapour pressure of the components in comparison with the corresponding pure substances occurs not only owing to the change in the relative number of evaporating particles. Here, in addition, we have to deal with the circumstance that the forces of attraction between different particles (*A*-*B*) differ from the forces of interaction between identical particles (*A*-*A* and *B*-*B*). It is clear that if, for example, the forces *A*-*B* exceed the forces *A*-*A* and *B*-*B*, they will prevent evaporation of particles from the solution, and the saturated vapour pressure will be lower than follows from Raoult's law. On the other hand, it may also happen that the presence of particles of *B* reduces the forces of attraction *A*-*A*, and the presence of particles of *A* reduces the forces of attraction *B*-*B*. In this case, particles of both the components will evaporate from the solution more easily than from the pure substances, and the vapour pressure over the solution will be greater than is required according to Raoult's law.

Thus, deviations from Raoult's law are always observed in real solutions, and these deviations can be used to assess the nature of the forces of interaction between the particles of the solution.

**Henry's Law.** We have seen that Raoult's law as applied to ideal solutions relates equally to the solvent and the solute. According to this law,

the saturated vapour pressure of a solute $p_2$ over a solution is proportional to the concentration of this substance in the solution:

$$p_2 = kx_2 = p_2^\circ x_2 \tag{7.66}$$

where $k$ is a constant equal (for ideal solutions) to the saturated vapour pressure over the pure substance at the same temperature. The quantity $k$ is called *Henry's coefficient* or the *Henry law constant*. The subscript "2" in Eq. (7.66) stands for the solute (it is conventional practice to use the subscript "1" for the solvent and "2" for the solute).

Here we are dealing with a saturated vapour. This means that the number of particles passing from the solution into the vapour equals the number of them returning from the vapour to the solution. Hence, we can speak with equal right of evaporation of the solute from the solution and of dissolving of its vapour in the solvent. If we consider the last process, i.e. dissolving of the vapour (or in general of any gas) in the liquid, then Eq. (7.66) should be rewritten in the form

$$x_2 = \frac{1}{p_2^\circ} p_2 = k' p_2$$

This means that *the concentration of a gas dissolved in a liquid is proportional to its pressure over the solution.*

This statement is called *Henry's law* (W. Henry, 1803). The law is strictly true only for ideal solutions, i.e. for those for which Raoult's law holds. Deviations from Henry's law are always observed in real solutions.

**Boiling Point of Solutions.** If a solute is not volatile and does not evaporate from a solution, the vapour over the solution consists only of solvent particles. It is clear from what has been said above that the pressure of such a saturated vapour over a solution is less than the pressure of the same vapour over the pure solvent at the same temperature, and this diminishing of the vapour pressure is determined by Raoult's law.

A result of such a change in the saturated vapour pressure is a change in the boiling point of the solution in comparison with that of the pure solvent. We already know that the boiling point is the temperature at which the saturated vapour pressure of a liquid equals the external pressure (for instance atmospheric pressure). And since the saturated vapour pressure over a solution is less than over a pure substance, the solution must be heated to a higher temperature for this pressure to become equal to the external one. This means that the boiling point of a solution is higher than that of the pure solvent.

Using Raoult's law determining how the vapour pressure over a solution lowers and the Clausius-Clapeyron equation relating the boiling point of a liquid to the external pressure, we can get the following equation for the lowering of the boiling point of a solution:

$$\Delta T_b = \frac{RT^2}{L} x_2 \tag{7.67}$$

where $\Delta T_b$ = difference between the boiling points of the solution and the pure solvent
$L$ = molar latent heat of vaporization of the pure solvent
$x_2$ = concentration of the solution (the mole fraction of the solute).

If we use the molality instead of the molar concentration, it is easy to see that Eq. (7.67) becomes (for weak solutions):

$$\Delta T_b = \frac{RT^2 \mu m}{1000L} \tag{7.68}$$

where $\mu$ = molecular weight of the solute
$m$ = molality of the solution.

This equation can be used for determining the molecular weight $\mu$ of the solute according to measurements of the change in the boiling point of the solution in which it is contained (ebullioscopy).

Equations (7.67) and (7.68) are especially well obeyed for weak solutions.

## 7.15. OSMOTIC PRESSURE

Let us assume that the same vessel contains a solution and the pure solvent in contact with each other. The particles of the solute will obviously pass from the solution into the solvent, and this process of diffusion will terminate only when equilibrium is achieved, i.e. when the solute is uniformly distributed throughout the entire volume of the solvent. In exactly the same way, if two solutions having different concentrations are in contact instead of a solution and the pure solvent, in this case too diffusion of the solute particles from the more concentrated to the more dilute solution will occur until the concentration becomes identical throughout the entire volume. The solute expands, as it were, and tends to occupy the entire accessible volume of the solvent in exactly the same way as a gas expands in order to occupy the entire volume placed at its disposal.

Similar to the way in which a gas exerts a pressure on the walls of a vessel and in expansion can do work of moving a wall if it is movable (a piston), a solute can also exert a pressure on the partition separating a solution and the pure solvent or two solutions having different concentrations (the difference between the concentrations here plays the same part as the difference between pressures in gases). This pressure can be observed if we place between the solution and the pure solvent a *semipermeable membrane*, i.e. a membrane or partition through which the solvent easily passes, but the solute does not pass (Fig. 136). The solvent will therefore pass into the solution, and the level of the liquid in the part of the vessel containing the solution will rise. The solute particles, as it were, tend to move the membrane through the solvent. What is actually displaced, however, is not the rigidly secured membrane, but the level of the liquid (if it were possible to make a semipermeable movable piston, the latter would be displaced).

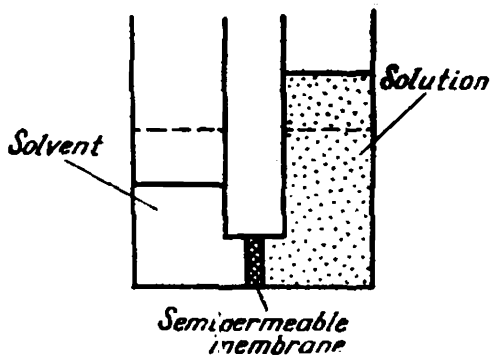



Fig. 136

The pressure exerted by the solute on the semipermeable membrane is called *osmotic pressure*, and the penetration of the solvent into the solution due to this pressure is called *osmosis*. The level of the solution liquid will rise until the appearing hydrostatic pressure is equal to the osmotic pressure. The level can be kept from rising if an external pressure is applied to the solution. The value of this pressure needed to ensure equality of the levels at both sides of the membrane is obviously equal to the osmotic pressure.

Experiments show that the osmotic pressure is proportional to the concentration of a solution and inversely proportional to its volume. It also depends on the temperature. J. van't Hoff showed (1887) that the relationship between these quantities has the form

$$\pi V = nRT \tag{7.69}$$

where $\pi$ = osmotic pressure
$V$ = volume of the solution
$n$ = number of moles of the solute
$R$ = molar gas constant
$T$ = absolute temperature.

The law expressed by this equation is called the *van't Hoff law*.

The complete similarity between the equation of the van't Hoff law and the equation of state of ideal gases shows that the solute particles in a dilute solution behave like the molecules of an ideal gas so that the van't Hoff law can be worded as follows: *the osmotic pressure exerted by a solute equals the pressure which this solute would exert in the gaseous state in the same volume and at the same temperature.*

The osmotic pressure, naturally, does not depend on the kind of semipermeable membrane or on the kind of solvent. It is obvious that any solutions having the same molar concentration exert the same osmotic pressure.

The similarity between the behaviour of a solute and an ideal gas is due to the circumstance that in a greatly dilute solution the solute particles do not interact with one another, just like the particles of an ideal gas do not interact.

It must be noted that the van't Hoff law does not hold when the solute upon dissolving decomposes into ions (dissociates). This, consequently, relates to all solutions of acids, salts, and alkalies (electrolytes).

Osmotic pressure plays a great part in the life of animals and plants. It determines to a considerable extent the distribution of water and substances dissolved in it in the tissues. This is connected with the circumstance that the envelopes of many organs are semipermeable membranes.

CHAPTER 8

# LOW TEMPERATURES

The continuous chaotic thermal movements which the particles of any substance always participate in and whose intensity (energy) determines its temperature have an appreciable influence on all the phenomena occurring in the substance. They are a sort of background on which any processes within a substance are staged. This is exactly why virtually any property of a substance depends in some way or other on the temperature, i.e. on the intensity of the thermal movements of the particles in it.

It is quite natural that the investigation of the properties of a substance at very low temperatures when the molecular movements are weakened to a certain extent is of great interest. Only at low temperatures is it possible to study various phenomena in conditions when the constant background of the thermal movements does not affect them.

In low-temperature investigations, the body being studied is brought into contact with a body having a sufficiently low temperature, a so-called cooling agent or coolant. It is the task of low-temperature engineering to create such coolants. The latter are usually various liquefied gases in the state of boiling. They are especially convenient because contact with the body being cooled does not change their temperature, but only results ina more intensive vaporization. It is exactly the liquefaction of gases that opened up the region of low temperatures for investigation, including the lowest ones close to absolute zero.

Below we shall briefly deal with the physics and technique of the liquefaction of gases.

## 8.1. LIQUEFACTION OF GASES

The van der Waals equation of state of real gases shows that any gas can be transferred to the liquid state, but first the gas must be cooled to a

temperature below the critical one. Carbon dioxide gas, for example, can be liquefied at room temperature because its critical temperature is 31.1 °C. The same can also be said about other gases such as ammonia and chlorine (see Table 13).

But there are gases that cannot be liquefied at room temperature no matter what pressure is applied to them and what densities they are brought up to. Such gases include, for example, air (and also its constituent parts — nitrogen, oxygen, and argon), hydrogen, and helium, whose critical temperatures are considerably lower than room temperature. Prior to the discovery of the critical temperature (C. Cagniard de la Tour, 1822), they were even considered to be permanent gases, i.e. ones in general incapable of being liquefied.

To liquefy such gases, they must first be cooled at least to a temperature somewhat lower than the critical one after which the gas can be transferred into the liquid state by increasing the pressure. It is more convenient to store gases liquefied in this way under atmospheric pressure (in an open vessel), but in this case their temperature must be still lower — it should have such a value at which the pressure corresponding to the horizontal section of an isotherm of a real gas equals 1 atm. Such an isotherm for nitrogen corresponds to the temperature 77.4 K whereas the critical temperature of nitrogen is 126.1 K. The corresponding figures for oxygen are 90 and 154.4 K, for hydrogen 20.5 and 33 K and, finally, for helium they are 4.4 and 5.3 K. We have mentioned these four gases because they are widely used in practice, both as coolants for obtaining low temperatures and for other purposes.

The above values of the critical temperatures and the final temperatures to which the gases being liquefied must be cooled show that the cooling required is quite considerable and nothing like it is encountered anywhere in nature (in the conditions of the Earth). Usually two methods are used (either separately or jointly) to achieve such great cooling, and we shall consider them on the following pages.

The first of them is connected with the use of the so-called Joule-Thomson effect.

## 8.2. JOULE-THOMSON EFFECT

It was indicated in Chap. 2 that the expansion of an ideal gas into a vacuum is not attended by a change in its temperature. The slight change in the temperature observed in accurate measurements is explained by the *non-ideal nature* of the gas. The following modification of the gas expansion experiment proposed by J. Joule and W. Thomson makes it possible to achieve a noticeable change in the temperature of a gas, particularly cooling, owing to its non-ideal properties.

A gas at a sufficiently great, but constant pressure is forced to flow through a thermal-insulating porous partition. This means that the flow of the gas occurs *adiabatically*.

The hydrodynamic resistance of the partition leads to the fact that the gas loses part of its pressure on it and leaves the partition at a lower pressure. The gas therefore expands or, as is said in engineering, is *throttled*. Any device resisting the flow of a gas is called a throttle. In technical installations for the cooling of gases, sufficiently narrow nozzles are often used instead of a porous partition.

For the flow of a gas to be *steady*, i.e. to occur at constant values of the pressure at both sides of the throttle, it is necessary to have a pump (compressor) that would keep these pressures constant. The compressor performs the external work of compression of the gas spent to overcome the resistance of the throttle. This is the difference between throttling and the expansion of a gas into a vacuum when the external work equals zero.

We shall show that for a *real gas* the Joule-Thomson process, i.e. the throttling process, generally speaking, should be attended by a change in its temperature. An identical expansion of an *ideal gas* will not cause its temperature to change.

*The phenomena of the change of the temperature of a gas upon its adiabatic expansion by throttling from one constant pressure to another one is called the Joule-Thomson effect.*

The change in the temperature of a real gas in the Joule-Thomson process is explained by the fact that the expansion of the gas is accompanied by an increase in the distance between the molecules, and, therefore, internal work is performed against the forces of interaction between the molecules. The kinetic energy of the molecules and, consequently, the temperature of the gas change at the expense of this work. In an ideal gas, where the forces of interaction between the molecules equal zero, the Joule-Thomson effect is absent.

The Joule-Thomson effect is characterized quantitatively by the Joule-Thomson coefficient $\mu_J$ that is determined by the ratio of the change in the temperature of the gas $\Delta T$ to the change in its pressure $\Delta p$:

$$\mu_J = \frac{\Delta T}{\Delta p} \tag{8.1}$$

Let us calculate the Joule-Thomson coefficient using the thermodynamic relationships derived in earlier sections. These calculations are a useful illustration of how thermodynamics is employed to solve concrete problems. But before starting our calculations, let us analyse the Joule-Thomson process in greater detail. For this purpose, we shall represent the process somewhat schematically.

Assume that a definite mass, for instance one mole of a gas, flows from the left to the right through porous partition $L$ (Fig. 137) placed in a thermally insulated cylinder.

Let one mole of the gas occupy the volume $V_1$ between partition $L$ and point $M$ at the left (see Fig. 137*a*), and after it passes through the partition, i.e. after expansion — the volume $V_2$ between the partition and point $N$ at the right (see Fig. 137*b*). For clearness, let us mentally place at point $M$ piston $C_1$ whose motion to the right causes the gas to flow through the partition at a constant pressure $p_1$. After passing through the partition, the same gas moves an imaginary piston $C_2$ resisting a back pressure (also constant) $p_2$ up to position $N$. Actually the part of pistons $C_1$ and $C_2$ is played by the compressor mentioned above.

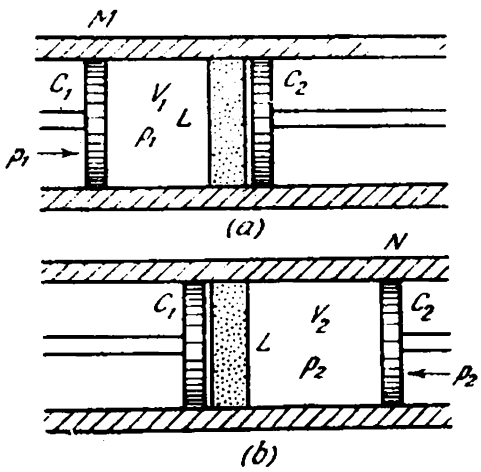



Fig. 137

Let us calculate the external work done by the gas. When piston $C_1$ is moved from position $M$ to partition $L$, the volume of the gas changes from the value $V_1$ to zero. At a constant pressure, the work done equals the product of this pressure and the change in the volume. Hence, the work of moving one mole of the gas to the left of the partition equals $-p_1V_1$. For the same reasons, the work done by the gas to the right of the partition equals $p_2V_2$. The total work $\Delta W$ of gas expansion is

$$\Delta W = p_2V_2 - p_1V_1$$

According to the first law of thermodynamics, the work done by a gas must equal the change in its internal energy with the reverse sign because the expansion process has been conducted adiabatically so that $\Delta Q = 0$. Therefore, if $U_1$ and $U_2$ are the internal energies of a mole of the gas before and after its expansion, then

$$p_2V_2 - p_1V_1 = U_1 - U_2 \quad \text{or} \quad U_1 + p_1V_1 = U_2 + p_2V_2$$

The function $U + pV = H$ is called the *heat function* or *enthalpy* of a gas. It is a function of state which in an isobaric process plays the same part as the internal energy $U$ does in an adiabatic process or the free energy $A$ in an isothermal process. Hence, the Joule-Thomson process takes place so that the enthalpy of the gas remains *constant* at both sides of the partition (throttle):

$$d(U + pV) = 0 \tag{8.2}$$

For an ideal gas, both the internal energy and the product $pV$ depend *only on the temperature* (they are proportional to $T$). Consequently, the

enthalpy $H = U + pV$ depends only on the temperature. The equality of the enthalpies of an ideal gas at both sides of the partition simultaneously indicates equality of the temperatures. Hence, *the Joule-Thomson coefficient for an ideal gas equals zero.*

For a real gas, as we know, the internal energy depends not only on the temperature, but also on the volume $V$ occupied by the gas [see, for instance, Eq. (6.46)]. Therefore for real gases, equality of the enthalpies does not yet point to equality of the temperatures.

Indeed, experiments show that most gases (nitrogen, oxygen, carbon dioxide, etc.) *cool* when throttled at room temperature. But such gases as hydrogen and helium *become heated* in the same conditions. This means that in the first case the Joule-Thomson coefficient $\mu_J = \Delta T/\Delta p$ is positive (when $\Delta p < 0$ and $\Delta T < 0$), and in the second case is negative.

It must also be noted, finally, that the Joule-Thomson process is essentially irreversible, consequently, it is attended by an increase in the entropy, $dS > 0$.

It is not difficult to calculate the Joule-Thomson coefficient after the above discussion.

Equation (8.2) can be rewritten in the form

$$d(U + pV) = dU + p\,dV + V\,dp = 0$$

but from Eq. (6.34) we have $dU + p\,dV = T\,dS$. Hence,

$$T\,dS + V\,dp = 0 \tag{8.3}$$

Now we must express the change in the entropy $dS$ through the change in the temperature $dT$ and the change in the pressure $dp$. This was done in Chap. 6, where it was shown [see Eq. (6.41)] that

$$dS = \frac{C_p\,dT}{T} - \left(\frac{\partial V}{\partial T}\right)_p dp$$

Using this value of $dS$ in Eq. (8.3), we get

$$C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_p dp + V\,dp = 0 \tag{8.4}$$

whence we get the Joule-Thomson coefficient interesting us:

$$\mu_J = \frac{dT}{dp} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} = \frac{V}{C_p}(\alpha T - 1) \tag{8.5}$$

where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ is the cubic expansion coefficient [Eq. (1.16)].

All the quantities in Eq. (8.5) can be determined if we know the equation of state for the gas being studied, and at any rate they can be measured. Consequently, the coefficient $\mu_J$ can be determined.

Inspection of Eq. (8.5) shows that the sign of the coefficient $\mu_J$ depends on the value of $\alpha T$. When $\alpha T > 1$, we have $\mu_J > 0$, and when $\alpha T < 1$, we have $\mu_J < 0$.

We know that for ideal gases $\alpha = 1/T$ (see Sec. 1.5) and therefore $\mu_J = 0$, which we have seen earlier in this section.

For real gases, the value of $\mu_J$ may be either positive or negative. And what is more, for the same gas $\mu_J$ may be positive in one region of temperatures and negative in another. In other words, there is a temperature $T_i$ characteristic of a given gas at which the Joule-Thomson coefficient *changes its sign*. This temperature $T_i$ is called the *inversion temperature*.

If the state of a gas is described by the van der Waals equation, it will also be a simple matter to find the numerical value of the Joule-Thomson coefficient with the aid of Eq. (8.5). To do this, we must calculate the derivative $(\partial V/\partial T)_p$ in this equation.

Opening the parentheses in the left-hand side of the van der Waals equation (5.6), i.e.

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

we get

$$pV + \frac{a}{V} - \frac{ab}{V^2} - bp = RT$$

Differentiation of both sides of the latter equation with respect to $T$ at $p = \text{const}$ yields:

$$\left(\frac{\partial V}{\partial T}\right)_p \left(p - \frac{a}{V^2} + \frac{2ab}{V^3}\right) = R$$

Substituting for $p$ its value from Eq. (5.6), i.e. $p = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$, we get

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2}$$

whence

$$\mu_J = \frac{T\left(\dfrac{\partial V}{\partial T}\right)_p - V}{C_p} = \frac{V}{C_p}\,\frac{2a(V-b)^2 - bRTV^2}{RTV^3 - 2a(V-b)^2} = \frac{1}{C_p}\,\frac{\dfrac{2a}{RT}\left(1-\dfrac{b}{V}\right)^2 - b}{1 - \dfrac{2a}{RTV}\left(1-\dfrac{b}{V}\right)^2} \tag{8.6}$$

If the pressure of a gas is not very great (of the order of magnitude of 100 to 200 atm), then

$$\frac{b}{V} \ll 1 \quad \text{and} \quad \frac{2a}{RTV} \ll 1$$

and we can disregard these quantities in Eq. (8.6). Hence,

$$\mu_J \approx \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \tag{8.7}$$

A glance at this expression shows that the Joule-Thomson coefficient is positive as long as $2a/RT > b$ or $T < 2a/bR$. When $T > 2a/bR$, the coefficient $\mu_J < 0$, i.e. a gas becomes heated when it is throttled.

The inversion temperature $T_i$ is obviously determined by the equation

$$T_i = \frac{2a}{bR} \tag{8.8}$$

Comparing Eq. (8.8) with Eq. (5.10) for the critical temperature, i.e.

$$T_{cr} = \frac{8a}{27bR}$$

we get the following simple relationship between the inversion temperature and the critical temperature:

$$T_i = \frac{27}{4} T_{cr} = 6.75 T_{cr} \tag{8.9}$$

This relationship, which has been obtained by very rough approximation, is confirmed quite satisfactorily by experiments. At any rate, the lower the critical temperature $T_{cr}$, the lower is the inversion temperature $T_i$. For oxygen, for instance, the inversion temperature is 893 K ($T_{cr} = 154.36$ K). For hydrogen and helium, the inversion temperatures are 204.6 and 40 K, respectively (the critical temperatures are 33 and 5.2 K).

The circumstance that in the experiment of Joule and Thomson, which was run at room temperature, hydrogen heated upon expansion whereas other gases cooled is naturally not a peculiar property of hydrogen. Any gas will exhibit the same property if the experiment is run at a temperature that is higher than the temperature of inversion. We shall see below that the Joule-Thomson effect is used for cooling hydrogen and helium when they are being liquefied.

Let us now consider the second method of cooling gases also used for their liquefaction.

## 8.3. ADIABATIC EXPANSION OF A GAS WITH THE PERFORMANCE OF EXTERNAL WORK

In the throttling of a gas (the Joule-Thomson effect), cooling is achieved at the expense of *internal* work performed by the gas against the forces of attraction between its molecules. We know (see Sec. 3.14) that a gas is also cooled when it expands adiabatically, performing *external* work (for exam-

ple lifting a piston). This directly follows from the first law of thermodynamics expressed by Eq. (2.5), i.e.

$$dQ = dU + p\,dV$$

from which it can be seen that in adiabatic expansion ($dQ = 0$) we have

$$dU = -p\,dV$$

This means that a gas upon expanding and performing work reduces its internal energy and, consequently, its temperature. This relates equally to an ideal and to a real gases. As we indicated in Chap. 2, the reason why a gas cools when it performs external work is the diminishing of the velocities of its molecules when they strike the piston moving away from them, to which they give up part of their kinetic energy.

Generally speaking, cooling in adiabatic expansion with the performance of external work should be more effective than in throttling because adiabatic expansion is a reversible process (or, at least, a process that can be reversible) whereas the Joule-Thomson effect is an irreversible process. We have already learned that the reversibility of the processes in a machine ensures a greater efficiency. True, this conclusion relates to a machine converting heat into mechanical work, and not to a refrigerating machine. But everything said about the efficiency of a heat engine completely relates to refrigerating machines which may be considered as devices that are reversed heat engines.

We must remind the reader that in a refrigerating machine heat is taken from a cold body and transferred to a hotter one. Here mechanical work is done at whose expense this transfer of heat takes place. We know that such a process cannot proceed spontaneously. The "hot" body for a refrigerating machine is the surrounding medium, which is the heat sink for a heat engine. The heat from the body to be cooled is transferred to it.

A refrigerating machine is thus an inverted heat engine. We must consider the efficiency of a refrigerating machine to be the ratio of the quantity of heat $Q$ taken away from the body being cooled to the quantity of work $W$ done, i.e.

$$\beta = \frac{Q}{W} \tag{8.10}$$

The quantity $\beta$ is called the *refrigerating factor* (or the *coefficient of performance*). It is easy to show that for a refrigerating machine working according to the Carnot cycle the refrigerating factor is

$$\beta = \frac{T_1}{T_2 - T_1} \tag{8.11}$$

where $T_1$ = temperature of the body being cooled

$T_2$ = temperature of the body which the heat is transferred to.

It is natural that the refrigerating factor may be greater than unity. A machine that spends the least work for removing a given quantity of heat from the body being cooled is considered to be the best one for the purpose.

Just like the object of a heat engine — the performance of work — is achieved upon the expansion of a gas, so is the object of a refrigerating machine — cooling — achieved upon the expansion (adiabatic) of a gas. Therefore, the most important part of such a machine is the part in which expansion of a gas occurs. It is called a *gas expander*. These machines are of the most diverse design.

For a gas to be subjected to expansion (in a gas expander), it must first be compressed in a compressor. The work done by the compressor is exactly the work at whose expense it becomes possible to transfer heat from a cold body to a hot one. But compression of a gas is attended by its heating, which naturally reduces the effectiveness of the following cooling in expansion. Therefore, the heat liberated in compression is removed (for instance with the aid of running water) so that the process of compression may be considered isothermal.

From the thermodynamic viewpoint, the essence of the operation of the refrigerating machine we are considering that uses the adiabatic expansion of a gas can be seen most clearly from a diagram of the temperature dependence of the entropy. Figure 138 shows such a diagram at constant pressure for two different pressures — a high pressure $p_1$ and a low one $p_2$.

It is easy to see that the curves properly show the features of entropy as a measure of disorder. It is clear that the disorder (and, consequently, the entropy) is the greater, the higher is the temperature, and the smaller, the greater is the pressure. This is what is shown by the graph in Fig. 138.

The process of isothermal compression from the pressure $p_2$ to $p_1$ is depicted in Fig. 138 by vertical straight line $AB$ (the entropy diminishes). Horizontal straight line $BC$ corresponds to reversible adiabatic expansion from the pressure $p_1$ to $p_2$ because the entropy remains constant in this process. Examination of Fig. 138 shows that expansion is attended by lowering of the temperature from $T_2$ to $T_1$. This means that the growth in the entropy due to expansion is compensated, as it were, by its reduction attending cooling.

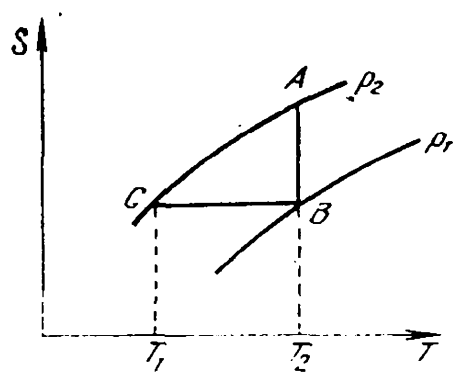


Fig. 138

The cooling of a gas by expanding it in a gas expander which we have just considered is used, like the Joule-Thomson effect, for lowering the temperature of gases having low critical temperatures before they are liquefied. Customarily, expansion in a gas expander serves only for preliminary cooling of the gases being liquefied to the lowest possible temperature (at any rate to below the critical temperature). The liquefaction itself

is achieved by throttling the already cooled gas. It is naturally possible to liquefy a gas in the gas expander itself without resorting to throttling, but this creates very strenuous conditions of machine operation at very low temperatures of the gases being liquefied. Therefore, in refrigerating plants using the method of adiabatic expansion in a gas expander, it is combined with the throttling method.

We shall now consider some examples of machines using the methods of cooling described above — the Joule-Thomson method and the method of adiabatic expansion with the performance of external work.

## 8.4. LIQUEFACTION OF GASES WITH THE USE OF THE JOULE-THOMSON EFFECT (THE LINDE METHOD)

The first machine ever constructed for the liquefaction of gases (air) on an industrial scale (K. Linde and W. Hampson, 1895) used the method of throttling to cool the gases to below their critical temperature and then liquefy them. At present, installations with expansion in gas expanders are mainly used for this purpose. But we shall nevertheless describe here how the Linde machine functions because in addition to the use of the Joule-Thomson effect it employed an important design principle of *counterflow heat exhange* which at present is also used in some form or other in all liquefying machines.

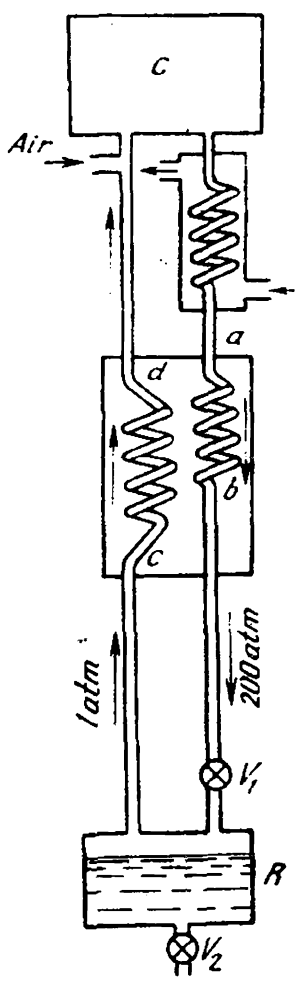


Fig. 139

The Linde machine is shown schematically in Fig. 139.

Air enters compressor $C$ where it is compressed to 200 atm. After this it passes through a coil cooled by running water where it gives up the heat liberated in compression. Thus, the further path to liquefaction is travelled by a compressed gas having the same temperature as it did before compression. This gas next passes through coil *ab* to throttle valve (cock) $V_1$ and expands through it into receiver $R$ to a pressure of 1 atm. During this expansion, the gas cools somewhat, but not enough to be converted into a liquid.

The cooled but not liquefied gas is then returned via coil *cd*. The two coils *ab* and *cd* are so arranged relative to each other that thermal contact exists between them and also between the portions of the gas passing along them. As a result, the gas that has undergone expansion and cooling cools the portion of compressed gas flowing toward it, which is still to expand through valve $V_1$. This is the principle underlying the method of counterflow heat exchange. It is obvious that the second portion of the gas will approach expansion

valve $V_1$ having a lower temperature than the first one, and after throttling it will lower still more. After passing in turn through the heat exchanger, this already twice cooled gas will again absorb heat from the new opposing portion of compressed gas, and so on. Thus a colder and colder gas will be supplied to the valve. In some time after operation of the machine has begun, the gradual cooling of the gas by the cold opposing streams will result in the fact that the gas during the next throttling will begin to partly liquefy and accumulate in receiver $R$ whence it can be drained off through cock $V_2$ into a Dewar flask.

The following approximate temperatures are observed at different parts of the machine after the process of its operation becomes steady: 293 K (room temperature) at the entrance to coil *ab*; 170 K at the exit from this coil; 80 K after throttling; 80 K at the entrance to coil *cd* (at point *c*); and room temperature at its exit. The pressure before the valve is 200 atm, and after throttling is 1 atm.

The device including the two coils *ab* and *cd* in which the gas is cooled by an opposing stream (counterflow) of the cooled gas is called a *heat exchanger.* In the Linde machine, the heat exchanger has the form of two tubes inserted one into the other and then given the shape of a coil. The high-pressure gas flows along the inner tube (Fig. 140). The counterflow of the cooled low-pressure gas passes along the outer tube around the inner one and thus cools the gas in the latter.

The above principle of counterflow is used in all refrigerating machines, although the designs of the heat exchangers have undergone considerable changes. In modern installations, they ensure better heat exchange and also make it possible to purify the gas being liquefied.

We shall depict heat exchangers in our diagrams by adjacent coils; the thick lines will show tubes for high-pressure gas, and the thin ones tubes for low-pressure gas.

We have already noted that machines of the Linde type are rarely used at present for compressing air. Machines of this type, however, whose action is based on the use of the Joule-Thomson effect, are still used for the liquefaction of hydrogen and helium. We shall describe as an example a machine of this kind used to liquefy helium.

Since the inversion temperature of the Joule-Thomson effect $T_i$ is very low for helium (about 50 K), it must first be cooled to a temperature below $T_i$. In the machine shown schematically in Fig. 141, helium is cooled by liquid hydrogen to a temperature of 14.5 K.

The helium compressed by a compressor to a pressure of 30 atm enters the machine in two streams along two tubes merging at point *O*. These two tubes are parts of two heat exchangers —*I* and *II*. In heat exchanger *I*, the helium is cooled by the counterflow of gaseous helium evaporating from receiver *R* that has already passed through heat exchanger *IV*. In heat

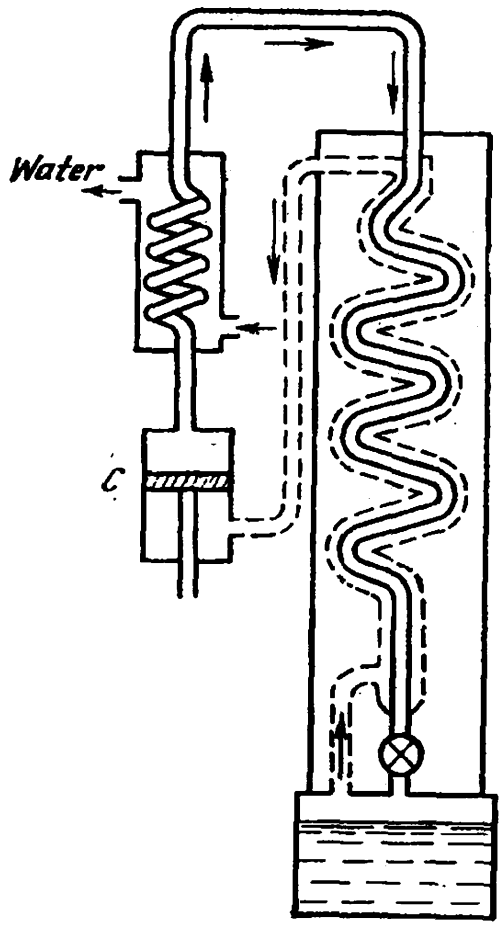



Fig. 140

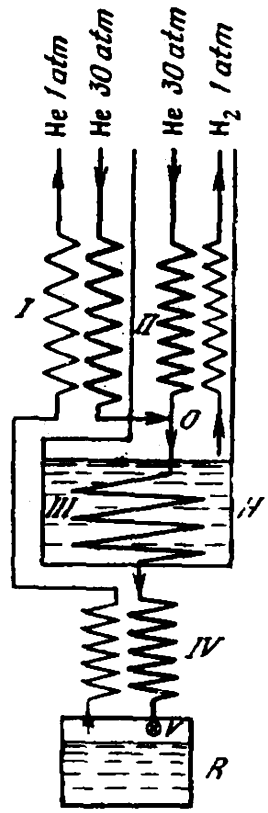



Fig. 141

exchanger *II*, the second part of the compressed gas is cooled by the counterflow of gaseous hydrogen evaporating from bath *H* with liquid hydrogen.

After merging at point *O*, the two streams together enter coil *III* passing through liquid hydrogen bath *H* and acquire its temperature (14.5 K). After passing through this bath, the helium enters heat exchanger *IV* where it is additionally cooled to a temperature of 5.8 K by the helium evaporating from the receiver. At this temperature, the helium is throttled through valve *V* and liquefies.

The entire apparatus is placed in a vacuum casing ensuring reliable thermal insulation.

The figures given above for the temperatures at different parts of the installation naturally relate to steady-state operating conditions. During acceleration of the machine, the temperature of the helium before being throttled is higher than 5.8 K (but naturally not higher than 14.5 K) because at this time the receiver does not yet contain any liquid helium. The machine has an output of about 10 litres of liquid helium an hour, which is a comparatively high figure.

## 8.5. LIQUEFACTION OF GASES BY ADIABATIC EXPANSION IN GAS EXPANDERS (THE CLAUDE PROCESS)

The use of gas expanders in which the gas is cooled upon adiabatic expansion with the performance of external work increases, as we have seen, the effectiveness of liquefying machines. In machines used for liquefying helium, the use of gas expanders also makes it possible to do without the preliminary cooling of the gas by liquid hydrogen — a substance that easily inflames and is an explosion hazard. Both these reasons resulted in the widespread use of gas expanders.

The first machine of this kind was built by G. Claude (1902) for liquefying air. The machine is depicted schematically in Fig. 142.

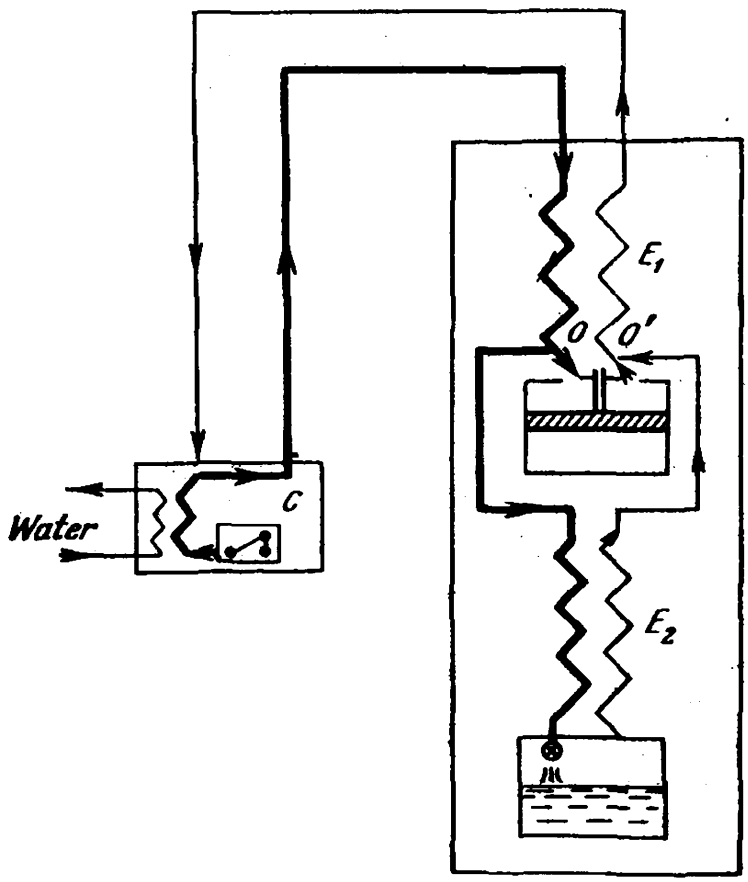



Fig. 142

The gas is compressed isothermally in compressor $C$ whence it is fed into heat exchanger $E_1$. Here it branches out into two streams (at point $O$). The first stream passes through heat exchanger $E_2$ to the throttle valve and is throttled with cooling at the expense of the Joule-Thomson effect; the second stream (it contains 80% of the gas) enters the gas expander, expands in it, performing work, and as a result is cooled. The cooled gas returns to heat exchanger $E_1$ from the gas expander, cooling the next portion of the compressed gas flowing in the opposite direction. It is joined at point $O'$ by the gas that was cooled as a result of throttling. Before this,

the latter while passing through heat exchanger $E_2$ also cooled the gas counterflow.

It can be seen from the above brief description that cooling in the gas expander is used for preliminary cooling before throttling.

In the first machine designed by Claude, the gas expander was a piston one. The work done in it by the compressed gas could be used for facilitating the operation of the compressor, for forced lubrication of the machine, etc.

The conditions characteristic for a Claude machine (liquefying air) are approximately as follows: the pressure at the compressor outlet is 40 atm, the temperature at the inlet to the gas expander (i.e. after cooling in heat exchanger $E_1$) is 200 K, and the temperature after expansion in the gas expander is 110 K at a pressure of 1 atm.

There are many different designs of machines of the Claude type for liquefying air. One of the most interesting of them is the machine designed by P. Kapitza in which the piston gas expander has been replaced by a turbine one. Another feature of this machine is the low pressure under which the gas enters the gas expander. It is only 6.5 atm. But in this machine almost all of the gas (and not 80% as in the Claude machine) passes through the gas expander. As a result of expansion in the turbine gas expander, the gas cools to 86 K and liquefies the part of the gas that has bypassed the expander. The liquid obtained is under an increased pressure and is throttled through the corresponding valve to a lower pressure.

Expanders (only piston ones) are also used in machines for liquefying hydrogen and helium. The first expander machine for liquefying helium was also built by P. Kapitza (1934). It was designed for the preliminary cooling of the helium with *liquid nitrogen* instead of liquid hydrogen. The failing cooling was provided by expansion in the gas expander. The liquefaction itself of the gas was performed by throttling.

When expanders are used in helium liquefying machines, a critical problem of lubrication appears because at the low temperatures created in such machines all lubricants solidify. The lubricant used in Kapitza's expander is the helium itself for which a gap of about 0.05 mm is left between the piston and the cylinder. Later S. Collins (1947) constructed an expander machine for the liquefaction of helium after improving Kapitza's expander (the gap in Collins's expander does not exceed 10 microns). Collins's machine is provided with a two-stage expander and can function without preliminary cooling of the helium. Its output is comparatively high — up to 10 litres an hour, and with preliminary cooling with liquid nitrogen up to 30 litres an hour.

## 8.6. SOME PROPERTIES OF LIQUEFIED GASES

The liquefied gases treated above — nitrogen, oxygen, hydrogen, and helium — permit us to obtain low temperatures within temperature intervals ranging from their boiling points at atmospheric pressure to their

freezing points. The latter can be reached by evacuating the vapour over the relevant liquid (an exception is helium that does not freeze upon any cooling). These gases cannot serve as coolants in the solid state because it is difficult to create a reliable thermal contact between them and the bodies being cooled.

Table 18 gives data showing what temperature intervals are covered by these liquefied gases. It also contains other data relating to them.

*Table 18*

**Thermodynamic Parameters of Selected Liquefied Gases**

| | $N_2$ | $O_2$ | $H_2$ | $He^4$ |
|---|---|---|---|---|
| Boiling point at pressure of 1 atm, K | 77.32 | 90.12 | 20.39 | 4.21 |
| Freezing point, K | 63.14 | 54.36 | 14.04 | Does not freeze |
| Vapour pressure at freezing point, mbar | 129 | 1.50 | 75.8 | — |
| Density at boiling point at 1 atm, kg/m³ | 800 | 1150 | 71 | 125 |
| Heat of vaporization at boiling point at 1 atm, kJ/kg | 200 | 212.8 | 456.2 | 23 |
| Density in solid state, kg/m³ | 1026 | 1425 | 80 | — |

Inspection of the table shows that liquefied gases make it possible to directly obtain low temperatures within the following intervals:

from 63.14 to 77.32 K — liquid nitrogen,
from 54.36 to 90.12 K — liquid oxygen,
from 14.04 to 20.39 K — liquid hydrogen,
from 0.7 to 4.21 K — liquid helium (0.7 K is the lowest temperature achieved by evacuating the vapour of liquid helium $He^4$).

These liquefied gases can be used to obtain any intermediate temperatures, although this requires the employment of special devices that are sometimes very complicated.

These devices used for conducting investigations both within the temperature intervals given above and at higher temperatures are called *cryostats*. They make it possible not only to obtain any needed temperature, but also to keep it constant during the investigations. They are also provided with a thermometer for measuring the temperature.

Figure 143 shows a very simple cryostat for research in the region of liquid-helium temperatures.

It consists of two Dewar vessels placed one inside the other — inner vessel *A* and outer one *B*. The former is filled with liquid helium, and the latter with liquid nitrogen. Su h a nitrogen "environment" is needed to reduce the influx of heat from outside, which makes it possible to retard evaporation and thus prolong the "service life" of the liquid helium being used. The inner vessel is vacuum-tightly closed with a lid (sealing is ensured by rubber collar *c* enveloping the lid and the vessel). Tube *T* in the lid serves for evacuating the helium vapour, which makes it possible to change the temperature of the helium. By keeping the vapour pressure constant (with the aid of a special device outside of the cryostat not shown in the figure), we can also keep the temperature of the liquid constant. A pressure gauge (also not shown in the figure) connected to the cryostat through tube *M* serves for measuring the vapour pressure, and to assess the temperature of the liquid according to it. The body being studied placed into the liquid helium is fastened to the lid by means of thin-walled tubes of a material that conducts heat poorly.

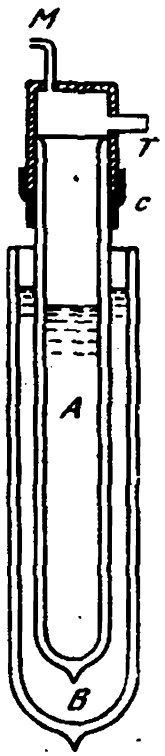


Fig. 143

## 8.7. EXTREMELY LOW TEMPERATURES

The data given in Table 18 show that liquefied gases make it possible to obtain temperatures as low as 4.21 K (liquid helium).

If we make liquid helium boil at a reduced pressure (for this purpose the vapour over it must be evacuated), its temperature can be lowered to about 1 K. The lowest temperature obtained in this way — the record — is 0.69 K. The further lowering of the temperature of the liquid helium by evacuating its vapour is virtually impossible because the vapour pressure of helium in this region of temperatures becomes very low. If at 0.7 K, the vapour pressure of helium is $2.2\times10^{-3}$ mm Hg, then at 0.5 K it becomes equal to $1.6\times10^{-5}$, and at 0.3 K to $3.2\times10^{-10}$ mm Hg. Bearing in mind the easiness with which liquid helium evaporates (its heat of vaporization is 23 kJ/kg), it is clear that the pumps cannot "have time" to evacuate the vapour to such small pressures.

Therefore to obtain still lower temperatures (they are called extremely low), another method is used — the so-called *magnetic method of cooling*. Its essence can easily be understood from the second law of thermodynamics.

A special kind of substances, the so-called paramagnetic salts, are used as the coolant in this method. They are complicated chemical compounds,

an example of which is the salt $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$ (ferric ammonium alum). These substances are remarkable in each of their molecules having a magnetic moment, i.e. behaving like a free tiny permanent magnet. In ordinary conditions, i.e. in the absence of a magnetic field, these microscopic magnets are oriented absolutely chaotically owing to the thermal motion which the molecules of the salt participate in (Fig. 144*a*). A definite entropy is connected with this magnetic disorder, as it is with thermal disorder.

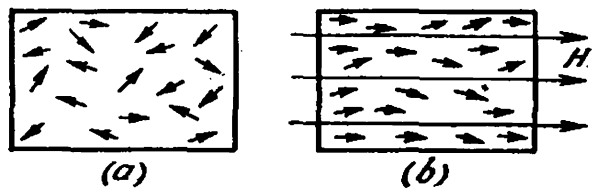



Fig. 144

If we place a paramagnetic substance in a magnetic field, the magnetic moments will partially turn in the direction of the field so that a certain order will set in in their arrangement (Fig. 144*b*). This process is called *magnetization*. Hence, the magnetic field results in diminishing of the degree of disorder (magnetic). Consequently, the entropy connected with it also decreases.

Let us now imagine that a paramagnetic substance is magnetized in *adiabatic conditions* (reversibly). We know that the entropy in these conditions remains constant. But since the magnetic part of the entropy diminishes in magnetization, its thermal part should correspondingly grow, i.e. the temperature should become higher. Conversely, if a preliminarily magnetized sample is *adiabatically* demagnetized, it should cool: the increase in the magnetic disorder due to demagnetization and, therefore, in the entropy connected with it should be compensated by a reduction in the thermal part of the entropy, and this is what does occur in cooling. Demagnetization plays the same part in the magnetic method as the expansion of a gas in its cooling.

An experiment with magnetic cooling is run as follows: first a paramagnetic salt is cooled with the aid of liquid helium to the lowest possible temperature. Next, without interrupting the contact of the salt with the liquid helium, it is magnetized in the strongest possible magnetic field. The heat liberated during the process is absorbed by the liquid helium so that magnetization is conducted in isothermal conditions. After this, the salt is isolated from the liquid helium and is demagnetized (adiabatically) by removing it from the magnetic field. As a result, the salt is cooled. This method permits investigators to achieve exceedingly low "record" temperatures — of the order of magnitude of hundred thousandths of a kelvin.

The cooled salt obtained in this way is used to cool other bodies being studied. There are different ways of creating a thermal contact between the salt and samples being studied.

## 8.8. PROPERTIES OF A SUBSTANCE AT LOW TEMPERATURES

Appreciable changes in the properties of a substance should naturally be observed at low temperatures when the intensity of thermal motion is weaker. In considering these changes, however, we must establish first of all what temperatures are to be considered low. It is not difficult to see that absolutely different temperatures should be considered "low" with respect to different substances and for different properties of these substances. For instance, if we are dealing with the properties of liquids, it is clear that there is no sense in speaking of temperatures that are lower than their freezing point $T_{fr}$ (the exclusive case of liquid helium will be described below). For water, for instance, room temperature can be considered quite low because its ratio to $T_{fr}$ differs only slightly from unity.

We do not have the possibility of describing all the features of the behaviour of substances at low temperatures here in sufficient detail. We shall therefore restrict ourselves to only a few general remarks on low-temperature phenomena and on the properties of various classes of substances in these conditions.

At the lowest temperatures — those obtained with the aid of liquid helium ("liquid-helium" temperatures) and moreover by the magnetic method — thermal motion is so slight that it does not play a great part in many cases. As a result, the complicated interactions between atoms and molecules are revealed that are due to their structure, as it were, and that at higher temperatures are completely or partly oncealed by the influence of thermal motion. And since atoms and molecules consist of particles obeying the laws of quantum mechanics, at temperatures close to absolute zero the quantum effects become quite appreciable, and some phenomena have a purely quantum nature. We shall treat one of these phenomena at the end of this chapter.

**Gases at Low Temperatures.** At conventional temperatures and pressures, gases can be considered to be ideal with a great accuracy. This means that the molecules of a gas behave as if they do not interact with one another at all, and therefore only the kinetic energy of thermal motion is ascribed to each molecule.

Actually, however, the molecules always interact with one another, and the molecules of a gas have potential energy in addition to kinetic energy. The potential energy is due to the forces of interaction and depends on the distance between the molecules. But at high temperatures when the kinetic energy of the molecules is great, the potential energy in comparison with it can be ignored, and the gas may be considered ideal. At a

low temperature, the relative part of the potential energy grows, and this causes the properties of the gases to deviate from ideal ones.

The law of corresponding states (Sec. 5.11) based on the reduced van der Waals equation (5.22), i.e.

$$\left(\pi + \frac{3}{\omega^2}\right)\left(\omega - \frac{1}{3}\right) = \frac{8}{3}\theta\tau$$

allows us to immediately determine whether a given temperature is high or low for a definite substance. Temperatures should obviously be considered low for which $\theta\tau = T/T_{cr}$ is close to unity or less than unity.

For example for water vapour ($T_{cr} = 647.1$ K), room temperature ($T = 290$ K) is a very low one because

$$\theta\tau = \frac{T}{T_{cr}} = \frac{290}{647.1} = 0.45$$

It can also be considered low for xenon ($T_{cr} = 289.1$ K):

$$\theta\tau = \frac{T}{T_{cr}} = \frac{290}{289.1} \approx 1$$

But for oxygen ($T_{cr} = 154.2$ K), room temperature should already be considered high because $\theta\tau$ is considerably greater than unity:

$$\theta\tau = \frac{T}{T_{cr}} = \frac{290}{154.2} = 1.88$$

The complicated nature of the forces of interaction between the molecules of a gas results in the fact that at low temperatures the van der Waals equation is insufficiently accurate. As we indicated in Chap. 5, for temperatures near to and below the critical one, an equation of state in the form of a series (for one mole) agrees the best of all with experimental data, i.e.

$$p = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\right) \tag{8.12}$$

In this equation the forces of interaction are reflected in the *virial coefficients* $B$, $C$, etc. depending on the temperature.

The first term of the series corresponds to the absence of forces of interaction. If we limit ourselves to this term, then as can be seen from Eq. (8.12), we get the equation of state for an ideal gas. The second virial coefficient $B$ reflects interactions in which two approaching molecules take part *(two-body interaction)*, the third coefficient $C$ takes into account interactions connected with the simultaneous approaching of three molecules, etc.

If the pressure of a gas is not too great, only the second term of the series, i.e. the second virial coefficient, is of significance because the probability of the meeting (collision) of three particles (and moreover four

and more) can become appreciable only at great densities of the gas. The second virial coefficient can be calculated exactly only with account of the structure of the atoms and quantum laws.

As we mentioned in Chap. 5, with definite approximations, Eq. (8.12) transforms into the van der Waals equation.

At the lowest temperatures, only two substances—hydrogen and helium—can be in the gaseous state with a noticeable pressure. All other gases at considerably higher temperatures freeze, and their vapour pressures become negligibly small. But in both "low-temperature" gases appreciable quantum effects are detected. Strictly speaking, the low critical temperatures of hydrogen and helium are in themselves quantum effects.

**Liquids at Low Temperatures.** The region of existence of the liquid state is restricted by the critical point from the side of high temperatures and by the freezing point from the side of low temperatures (the latter depends on the pressure — see Chap. 9). The changes in the properties of liquids when passing over to low temperatures (close to the freezing point) consist in a growth in the surface tension and in a great increase in the coefficient of internal friction (viscosity). In some substances, the increase in the viscosity even leads to the fact that the liquid acquires some features of a solid and first of all its ability to retain not only its volume, but also its shape.

We have already mentioned that at the lowest temperatures certain specific quantum phenomena are observed that cannot be considered the result of a gradual change in the properties of a substance with lowering of the temperature. These phenomena appear in a jump at a quite definite temperature and have no analogues at high temperatures. We have in mind the phenomena of superconductivity and superfluidity. The former consists in abrupt vanishing of electrical resistance in metals and is observed in quite a great number of pure metals and alloys. The latter relates to a single substance in nature — liquid helium.

In the following section we shall discuss this unusual property of liquid helium and the phenomena related to it.

## 8.9. LIQUID HELIUM

Liquid helium is remarkable first of all in that it is the coldest liquid in nature. Ordinary helium ($He^4$) consisting of atoms with an atomic weight of 4 has a critical temperature of 5.25 K. Hence, in the liquid state it can exist only below this temperature. Under a pressure of 1 atm, it boils at 4.21 K. The rare helium isotope with an atomic weight of 3 ($He^3$) has a still lower critical temperature. The latter equals 3.35 K, and under a pressure of its vapour equal to 1 atm liquid helium $He^3$ boils at 3.195 K.

All other substances already at considerably higher temperatures pass over into the solid state. Liquid helium, however, does not solidify even at temperatures still closer to absolute zero, and everything points to the fact that at absolute zero too the normal state of helium is the liquid one. This, however, does not mean that helium cannot be solid in general.

It can be transferred into the solid state only under an increased pressure which is the higher, the higher is the temperature. Even at absolute zero, a pressure of 25.27 atm would be needed for the freezing of helium.

The most important feature of liquid helium is the existence of two modifications of it that transfer into each other at 2.186 K (at this temperature the transition occurs at a vapour pressure of one atmosphere; at an increased pressure the transition temperature is lower). These two modifications are called He I and He II. The transition point from He I to He II and vice versa is usually called the *lambda* ($\lambda$) *point*. This name has been introduced owing to the shape of the curve showing the temperature dependence of the heat capacity of liquid helium which reminds one of the Greek letter $\lambda$ (Fig. 145). The jump of the heat capacity at the transition point is an important feature of this transition that distinguishes it from such transitions, for instance, as vaporization or melting, which are not attended by a jump in the heat capacity, but upon which the latent heat is liberated (see Chap. 9). The transition from He I o He II occurs without the liberation or absorption of latent heat.

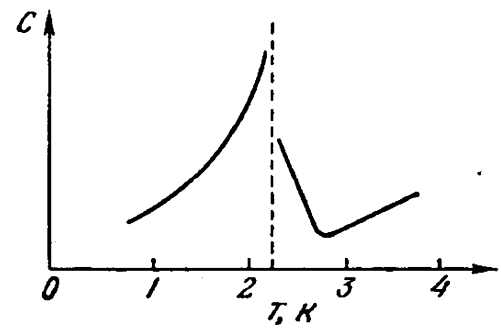


Fig. 145

Liquid He I, i.e. liquid helium above the lambda point, has normal properties for liquefied gases if we omit its very low temperature. It is a colourless liquid that violently boils with the abundant liberation of bubbles. The density of liquid helium is about 0.12 g/cm$^3$. The low-temperature modification, liquid He II, however, sharply differs in its properties both from He I and from all other liquids in nature. Even in appearance, liquid He II sharply differs from He I in that immediately after lowering of the temperature to below the lambda point, violent boiling stops together with the formation of bubbles. The reason for this phenomenon will be considered below.

**Liquid Helium II. Superfluidity.** The most striking feature of liquid helium II is its *superfluidity*. This property, which no other substance (not excluding the light isotope of helium) has, consists in that liquid He II when flowing through thin capillaries, slits, and the like experiences no friction. It flows as if its viscosity were zero (P. Kapitza, 1940).

We know that the viscosity (internal friction) is connected with the transfer of the momentum (impulse) from one layer of a flowing liquid or gas to another. This process occurs upon collision of molecules performing thermal movements with the simultaneous ordered motion of the entire liquid or gas as a whole.

Liquid He I, like any other liquid, has a viscosity, although a very low one, not greater than that of gaseous helium (about $2\times10^{-5}$ P). The flow of He I takes place in the same way as that of ordinary liquids. But upon

transition through the lambda point, the viscosity of helium sharply and suddenly drops at least a million times and becomes less than $10^{-11}$ P, i.e. it virtually equals zero (it should be remembered that the viscosity of water is $10^{-2}$ P). This means that liquid He II can freely flow through the thinnest capillaries, slits, and openings impermeable even for a gas. And it is exactly in the thinnest capillaries that the flow of liquid He II is characterized by laws radically differing from the laws of flow of conventional liquids.

For conventional liquids, the rate of flow is determined by the Poiseuille equation (7.18)

$$V = \frac{\pi r^4}{8\eta} \frac{\Delta p}{L}$$

where $V$ = volume of the liquid flowing through a section of a tube in one second
$\Delta p$ = pressure difference
$L$ and $r$ = length and radius of the tube, respectively
$\eta$ = viscosity of the liquid.

The rate of flow, consequently, grows with increasing $\Delta p$ and drops with increasing $L$ at a given viscosity.

The rate of flow of liquid He II in thin capillaries (from $10^{-4}$ to $10^{-5}$ cm) does not depend at all on the difference of pressures and on the length of the capillary, while with an increase in the thickness of the capillary the rate of flow diminishes instead of growing. This is exactly what shows that the flow of He II in such capillaries occurs without any viscosity. There is a definite rate of flow, the so-called *critical rate,* above which forces of friction begin to act and motion becomes viscous. The critical rate of flow grows with lowering of the temperature and only at the lowest temperatures does it become constant.

In wide capillaries (for liquid He II these are capillaries wider than $10^{-3}$ cm), liquid He II flows in a somewhat different way. Here there is no definite critical rate of flow above which forces of friction appear. The rate of flow in wide capillaries is proportional to the pressure difference. This means that if in narrow capillaries forces of friction are completely absent up to the critical rate of flow, then in wide capillaries such forces exist at almost all rates of flow, but they are sufficiently small not to hinder the growth in the rate of flow with increasing pressure difference. In wide capillaries, consequently, there is no flow of He II completely without viscosity. Here too the laws of flow greatly differ from the usual ones.

The remarkable property of superfluidity observed in He II cannot be explained with the aid of our conventional notions on the liquid state of a substance. We know that these notions relate to ordinary molecular systems in which thermal movements play a very great part. Liquid helium, on the other hand, exists only at the lowest temperatures when the energy of thermal movements becomes very small. It is not surprising that phenomena may occur in these conditions that are not observed at

higher temperatures. The property of superfluidity like all the other phenomena occurring at temperatures close to absolute zero was found to be a quantum effect, i.e. a phenomenon that can be explained only by quantum mechanics. L. Landau gave such an explanation in 1941.

The essence of Landau's theory consists in the following.

At absolute zero, liquid helium, like any other substance, is in a state in which the energy (and impulse or momentum) of its atoms cannot change. Hence upon motion relative to a body, for instance to the wall of a capillary (or, which is the same, upon the motion of the body relative to the liquid), the liquid cannot increase its impulse or energy (become excited) if the velocity (rate of flow) of this relative motion is less than a certain critical value. It is clear that a liquid whose particles cannot exchange their impulse (momentum) with other atoms has no viscosity, i.e. is superfluid.

At a temperature different from absolute zero, liquid helium becomes excited, but this occurs in such a way as if only part of the liquid were excited. The remaining part is not excited, i.e. continues to be in the state in which it would have been at absolute zero. Thus, at all temperatures above absolute zero and below the lambda point, liquid helium is, as it were, a mixture of two components — an excited and an unexcited ones. The former has viscosity, and the latter does not. Each of the components has its own density, but the total density of the liquid is naturally what is measured in experiments. If $\rho_n$ stands for the density of the normal component, $\rho_s$ for that of the superfluid component, and $\rho$ stands for the total density, then knowing the temperature dependence of $\rho$ and one of the components $\rho_n$ or $\rho_s$, we can determine the latter quantities.

It is possible to determine the relationship $\rho_n/\rho = f(T)$ experimentally. Therefore, knowing $\rho$ and $\rho_n/\rho$ and assuming that $\rho = \rho_n + \rho_s$, we can calculate the values of $\rho_n$ and $\rho_s$ and their temperature dependence. It is quite obvious that when the temperature changes from absolute zero to the lambda point, the value of $\rho_n$ changes from zero to $\rho$, and of $\rho_s$ from $\rho$ to zero: at absolute zero the entire liquid is superfluid, and above the lambda point it is all normal, viscous. From this viewpoint, the transition from He I to He II consists in that a superfluid component appears in normal liquid helium whose amount grows with further lowering of the temperature. Liquid helium is a substance that can actually be observed, as it were, in conditions of absolute zero (which, as we know, is unattainable). And it is the only such substance in nature.

The picture of liquid He II which we have just described allows us to understand the features of the flow of this liquid through capillaries, also discussed above.

Indeed, the flow of liquid helium through the capillaries is accomplished, naturally, by both components of the liquid. But the normal component is subjected to the action of the force of friction whereas no such force acts on the superfluid component. The narrower the capillary, the smaller

is the part played by the normal component which in such capillaries is subjected to the greatest friction. In the narrowest capillaries, the normal component cannot virtually participate in the flow and it is non-viscous. In wide capillaries, on the other hand, the part played by the normal component becomes more noticeable, and completely non-viscous flow can no longer be observed. Owing to the presence of the superfluid component, however, the usual laws of hydrodynamics are nevertheless not obeyed in this case too.

It has been experimentally established recently that the phenomenon of superfluidity is also observed in liquid $He^3$. But this substance becomes superfluid only at a temperature of several millikelvins.

**Thin Films in Liquid Helium II.** Another phenomenon — the formation of a thin moving film of liquid He II on the surface of any solid body in contact with it — is closely related to the property of superfluidity of liquid helium described above.

This phenomenon consists in that when a body is partly submerged in liquid He II, and the upper portion of the body has a higher temperature than the liquid, a thin film of the latter rises along the unsubmerged part and reaches the part of the surface of the body where the temperature is above the lambda point. Here the major part of the film evaporates. Such a film naturally also forms on the walls of the vessel itself in which He II is kept, above its level. It must be noted that this film increases the area of the surface which the liquid helium evaporates from and makes it difficult to evacuate its vapour.

We have already indicated that a liquid helium film is mobile and moves in the direction where the temperature is higher. If the surface of a body has the same temperature over its entire length, however (below the lambda point), the unsubmerged part of the surface becomes covered with a stationary film.

The experiments shown schematically in Fig. 146 can serve as interesting examples of the formation and motion of a film of He II.

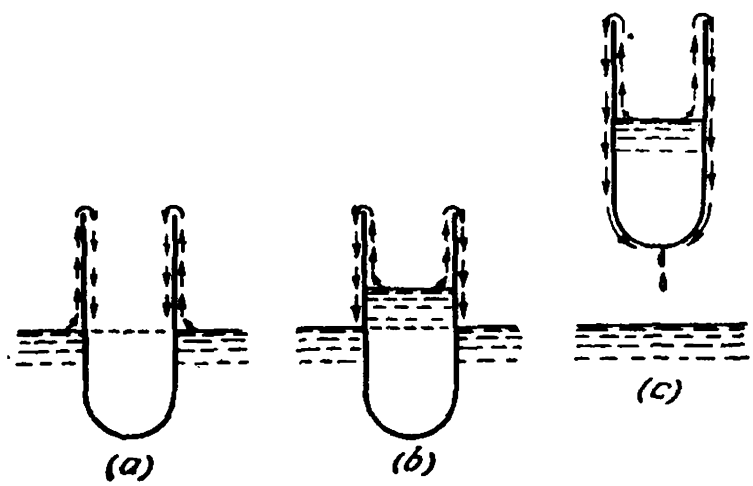



Fig. 146

If an empty test tube is submerged in liquid He II as shown in Fig. 146*a*, a film of the liquid will form on the outer wall of the tube. Moving upward along the wall, it penetrates into the tube and in the long run the liquid fills the tube so that the levels of the liquid in the tube and in the vessel in which it is submerged are the same.

If, on the contrary, a test tube is submerged in the vessel in which the level of the liquid is higher than in the vessel itself, the liquid helium, moving along the film formed on the inner surface of the tube, flows out of it until the levels of the liquid in the tube and in the vessel become the same (Fig. 146*b*).

Finally, if a test tube with liquid helium is suspended above the level of the liquid in the vessel (Fig. 146*c*), then owing to the film, the helium will travel along the walls of the tube and flow dropwise into the vessel until all of the helium flows out of the tube. Owing to the film, consequently, liquid helium cannot be stored in an open vessel all of whose parts are at a temperature below the lambda point.

Measurements have shown that the thickness of the film is about $2\times10^{-6}$ cm, i.e. about 100 layers of atoms (A. Kikoin and B. Lazarev, 1939).

It is interesting to note that the dependence of the rate of flow of liquid He II along the film on the temperature has the same form as for the rate of flow in narrow capillaries. Like the latter, the rate of flow (velocity) in a film does not depend on the difference in heights. Finally, for flow along a film as for flow through narrow capillaries, there is a definite critical rate of flow above which the flow stops being non-viscous. All this allows us to consider that the flow of liquid helium in narrow capillaries is not three-dimensional, but mainly occurs in the layer adjoining the walls, and it is exactly this flow which the superfluid component of liquid He II is responsible for.

The phenomenon of the formation of liquid films is in itself not an exclusive property of liquid He II. Many other liquids also form such films (kerosene or paraffin oil is the best known example). The cause of their formation are the forces of interaction between the particles of the liquid and solid. In ordinary liquids, however, viscosity prevents the formation and motion of films. But in helium, owing to superfluidity, a film is easily formed and moves without hindrance. Thus, the film phenomena in liquid He II are a consequence of its main feature—superfluidity.

**Thermomechanical Effect in Liquid Helium II.** We have already noted that liquid helium moves in a film when there is a difference of temperatures, and this motion is in the direction of the higher temperature. Such motion is a particular case of the so-called *thermomechanical effect,* which consists in that the presence of a heat flux in a thin capillary with liquid gives rise to a flow of the liquid in a direction opposite to this flux.

It is easy to observe this phenomenon in the simple device shown schematically in Fig. 147. A vessel with a heater inside and provided with a

capillary is submerged in a bath with liquid helium (the vessel in Fig. 147 is shown closed at the top, but it can also be open). When there is no current in the heater, the levels of the liquid in the vessel and outside of it are the same. But when the current in the heater is switched on, a heat flux is created through the helium in the capillary that is directed toward the liquid in the bath. A flow of liquid He II appears in the opposite direction, and the result is rising of the level of the liquid in the vessel.

The thermomechanical effect manifests itself especially vividly in the so-called *fountain effect*. The corresponding device for observing it is shown in Fig. 148. It is a long narrow capillary tube whose lower end widens out and is completely filled with a fine dark powder (for instance emery). The tube is immersed in liquid He II as shown in Fig. 148. If a beam of light is directed onto the bottom broad part of the tube so that the powder is heated, then the heat through the liquid helium filling the most minute ducts between the particles of the powder will be transmitted to the external helium. Hence, liquid helium will rush in the opposite direction from the

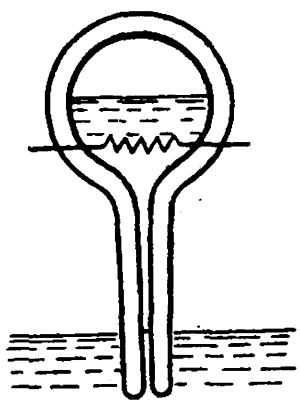


Fig. 147

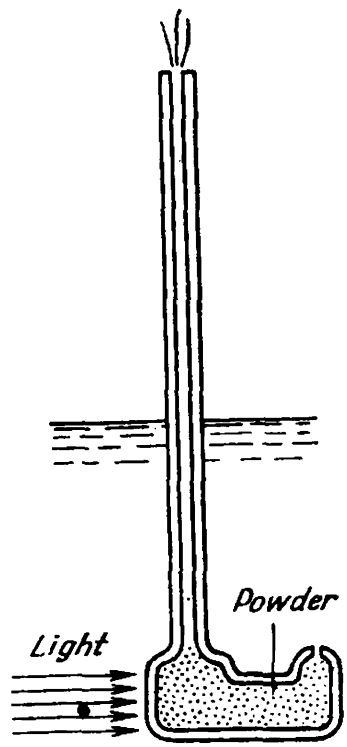



Fig. 148

bath into the tube and will emerge from its upper open end in the form of a fountain. This peculiar helium pump can lift the liquid to a height of up to 30 cm.

The thermomechanical effect can also be observed in a device in which the part of the thin capillary is played by a film of He II. Such a device is shown in Fig. 149.

An open cylindrical vessel provided with an electric heater is submerged in a helium bath. Owing to the film, it is rapidly filled with the liquid helium

so that the levels of the liquid within the vessel and outside of it are the same. If we now pass an electric current through the heater, heat will flow along the film toward the outer helium, and a flow of the liquid will appear in the opposite direction. As a result, the level of the liquid in the vessel will rise.

The remarkable phenomenon just described can also be explained by the property of superfluidity of liquid helium II. Indeed, heating of liquid

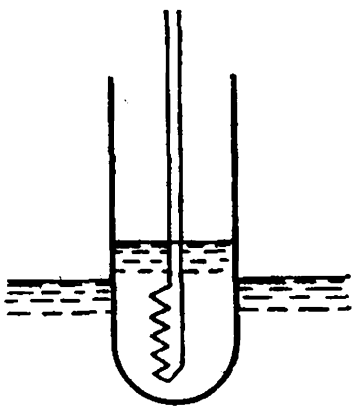


Fig. 149

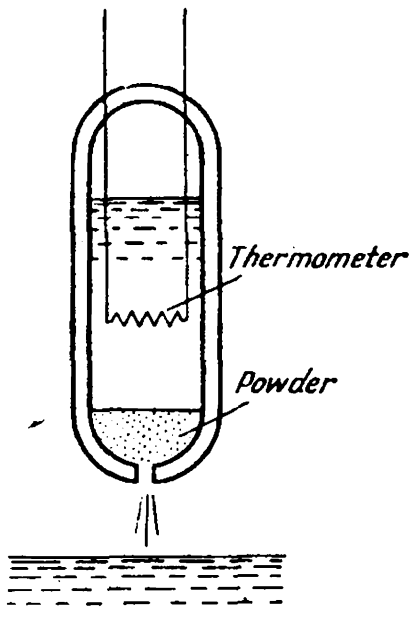



Fig. 150

He II results in the heated portion becoming poorer in the superfluid component. Therefore, a difference in the concentrations of this component is formed on both sides of the capillary or film. Since its viscosity equals zero, levelling out of the concentrations occurs through the capillary or film.

The thermomechanical effect thus reminds us somewhat of the phenomenon of osmosis, the capillary or film playing the part of the semipermeable membrane.

**Mechanocaloric Effect.** In addition to the thermomechanical effect which we have described above, the reverse effect is also encountered, which is called the *mechanocaloric effect*. It consists in that if liquid He II flows along a capillary or a film, then in the opposite direction to this *liquid flow* a *heat flux* will appear. As a result, a temperature difference appears between the part of liquid from which the helium is flowing out and the part into which it is flowing. This phenomenon can be observed, for instance, in the device shown in Fig. 150.

A closed (except for a small orifice) vessel provided with a resistance thermometer is submerged in a reservoir with liquid He II. The liquid helium penetrates into the vessel through the multitude of very minute capil-

laries in the powder covering the orifice in its bottom part and fills it up to the level of the liquid in the reservoir. If we now lift the vessel above the liquid in the reservoir, the liquid helium will flow out of the vessel through the minute channels in the powder. The thermometer will show an increase in the temperature of the liquid helium in the upper part of the vessel. The explanation is that the superfluid component, i.e. the part of the liquid that has no entropy and, consequently, is in conditions of absolute zero, mainly flows through the minute channels.

It is obvious that if we measure the temperature in the part of the reservoir into which the helium flows out from the vessel, it will be found to be lower. Thus, the "straining" of the liquid helium through the minute capillaries can, at least in principle, serve as a method for obtaining lower temperatures than that of liquid helium.

The mechanocaloric effect from the thermodynamic viewpoint is obviously the reverse of the thermomechanical effect.

**Thermal Conductivity of Liquid Helium II.** The thermal conductivity belongs to the properties of liquid helium which sharply change at the lambda point. Liquid He I is similar to gases as regards its thermal conductivity (and also its viscosity), and not only in the numerical value of the thermal conductivity coefficient, but also because for liquid helium, as for gases [see Eq. (3.48)], the ratio of the thermal conductivity coefficient $\lambda$ to the viscosity $\eta$ equals the specific heat capacity at constant volume $c_V$, i.e.

$$\frac{\lambda}{\eta} = c_V$$

But upon the transition through the lambda point, the thermal conductivity of liquid helium suddenly rises about $5 \times 10^6$ times so that the thermal conductivity of liquid helium is hundreds of times greater than in the best metal conductors of heat. Hence, liquid helium II is not only superfluid, but is also "superconductive".

It is easy to see, however, that the observed thermal conductivity is not at all thermal conductivity in the conventional meaning of the word and that heat is transferred in liquid He II by a more complicated mechanism than thermal conductivity. Indeed, we must have a temperature difference for the transfer of heat. But in liquid He II in the presence of a temperature difference, a flow of the superfluid component is initiated that is directed opposite to the flow of heat (the thermomechanical effect). The transfer of heat in liquid He II is therefore inevitably attended by the transfer of a mass of the liquid which naturally does not occur in conventional thermal conductivity. Hence, heat is transferred in liquid helium not so much by thermal conductivity as by original convection by special flows of the liquid.

The existence of such flows in the transfer of heat was shown very illustratively in experiments conducted by P. Kapitza (1941). One of them is shown schematically in Fig. 151.

A small glass vessel with a heater and a thermometer soldered into it terminates at the bottom in a thin tube. The vessel is put in a Dewar flask with liquid helium, and a light wing on a thin suspension thread is placed opposite the end of the tube. A mirror (not shown in the figure) that makes observation of the twisting of the thread possible is attached to it.

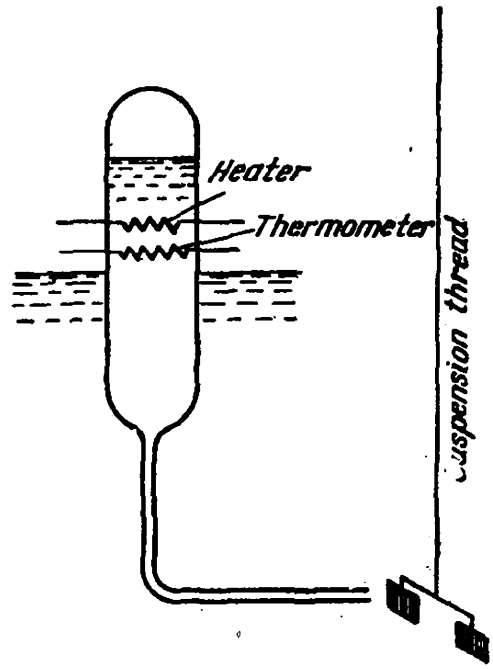



Fig. 151

When a current is passed through the heater and the liquid heats, the wing is seen to turn together with the suspension thread. This means that it is acted upon by a force that can be exerted only by the stream of liquid leaving the tube. This stream obviously consists of the normal component of liquid He II because the superfluid component, which is unable to change its impulse or momentum, also cannot induce a force.

The stream of the normal component leaving the vessel must naturally be compensated by the return stream of the superfluid component (apparently flowing along the layer in the tube adjoining its wall). But this stream directed toward the source of heat does not act on the wing and is not detected directly.

Thus, the transfer of heat in liquid He II is connected with complicated movements in the liquid, and it is exactly these movements that ensure the extraordinarily high apparent thermal conductivity of liquid He II. These movements apparently also explain the stopping of visible boiling of liquid helium upon passage through the lambda point.

It is natural that the character of the flow of the liquid and, consequently, heat transfer in liquid He II should depend on the thickness of the capillaries because in very thin tubes the flow of only the superfluid component is possible. Heat transfer should also depend on the rates of flow because at rates higher than the critical value the flow stops being non-viscous even for the superfluid component.

CHAPTER 9

# SOLIDS

## 9.1. INTRODUCTION

A solid is characterized by its ability to retain not only its volume, as is observed in a liquid, but also its shape. With a single exception (helium), all substances at sufficiently low temperatures pass over into the solid state. This means that when the velocities of thermal movements of the particles become small, the forces of interaction between them limit the movements of the atoms to such an extent that the body acquires the ability to retain its form and restore it after it has been changed by the action of an external force. The ability to retain their shape (elasticity of form) is the main external difference of solids from liquid and gaseous substances. In addition to this, solids have many other features distinguishing them from liquids. And these differences are in many respects deeper than those distinguishing liquids from gases.

This, however, relates not to all solids. Substances exist which as regards the feature of retaining their shape should be related to solids, but otherwise do not differ from liquids. These substances, called *amorphous*, include glass, various resins, and plastics. Amorphous substances behave like liquids with an anomalously great viscosity owing to which at ordinary or low temperatures they cannot flow. Upon elevation of the temperature, however, their viscosity diminishes, they gradually soften and acquire the ability to flow that is a usual property of liquids.

Unlike this, such softening does not occur in "genuine" solids although they pass over into the liquid state when the temperature rises. This transition occurs not upon gradual elevation of the temperature, but in a jump when a quite definite temperature — the melting point — is reached for a given substance. This is one of the important features distinguishing "genuine" solids from amorphous ones. This and other features of the solid state point to certain internal features in the structure of solids that are absent in liquids and amorphous bodies.

Thermodynamically, the state of a solid like that of a fluid is determined by the parameters of state which we already know — volume, pressure, and temperature. For an ideal gas, the equation relating these three parameters, i.e. the equation of state, was derived sufficiently strictly using definite assumptions on the properties and behaviour of gas molecules. For real gases and liquids, an accurate equation of state can no longer be obtained owing to the difficulties encountered when taking the forces of interaction between the particles into consideration. Here we had to be content with approximate equations, in particular the van der Waals equation. It is not surprising that these equations could not be directly used to explain and describe many phenomena in liquids.

The task is even more difficult for solids, and it is also impossible to write an equation of state for them in the explicit form.

The relationship between the parameters of state can, however, be established for separate concrete problems experimentally. But the equations obtained in this way are not universal. For example, experiments have given us the relationship between the volume of a body and its temperature at constant pressure, i.e. the form of the function $V = f(T)$. It describes the known phenomenon of the thermal expansion of bodies. Experiments also give us the relationship between the volume of a body and the pressure at constant temperature: $V = f(p)$. It describes all the possible deformations (strains) of a solid under the action of external forces. The laws of thermodynamics which naturally also hold for solids make it possible to find more complicated relationships between the parameters of state.

Owing to the exceedingly great diversity of the conditions, however, we cannot compile a universal equation relating $p$, $V$, and $T$ that would be able to give for the description of solids what, for example, the Clapeyron-Mendeleev equation (1.11) gives for an ideal gas.

We shall begin our study of the properties of solids with consideration of the features that distinguish them from fluids and of the properties that are a result of these features.

At present, it can be considered as an established fact that the properties of solids are mainly due to the atoms (or other particles) being arranged in them not chaotically as in fluids, but in a definite order characteristic of each substance. In a solid, such an ordered arrangement of the atoms extends throughout the entire volume of a body (the so-called *long-range order*). Such bodies with a regular arrangement of their particles are called *crystalline*. Only these bodies should be considered as solids. In amorphous and, evidently, in liquid bodies, the ordered arrangement of the particles extends only to the adjacent atoms (the so-called *short-range order*).

Atoms pass over to an ordered arrangement when a solid is formed because of the forces of interaction between them. Since a crystal forms by itself when a substance is cooled, the atoms become arranged in the crystal so that their potential energy in the field of the forces of interaction is minimum and the force itself equals zero.

The nature of the forces of interaction between atoms is well known. They are electrical forces of attraction and repulsion of positively and negatively charged particles (electrons and nuclei) present in each atom. These forces are very complicated — already because we have to do with the interactions of all the electrons and nuclei of all the atoms of a body. But matters do not even lie in the multiplicity of the forces, but in that, as it turned out, classical physics cannot describe them at all. Even such a simple case as the interaction of only the two atoms in a hydrogen molecule cannot be described and explained on the basis of classical physics.

Only quantum mechanics gives a solution of the problem, but this is beyond the scope of our course. We shall only note here that the dependence of the force of interaction $F$ of two atoms on the distance $r$ between them has the form shown in Fig. 152. At great distances, the atoms do not vir-

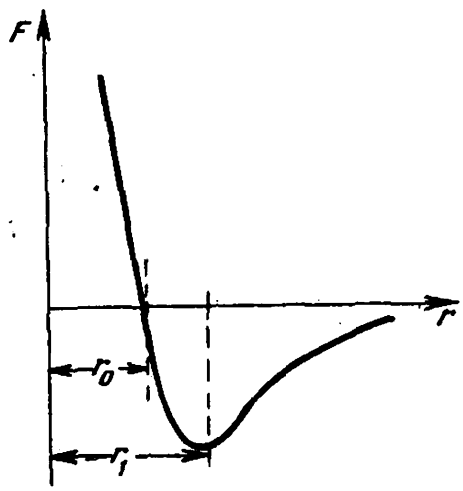



Fig. 152

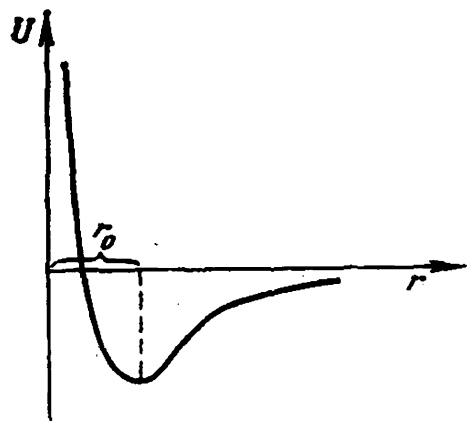



Fig. 153

tually interact with one another so that the force may be considered equal to zero. Diminishing of the distance $r$ is attended by the appearance of a force of *attraction* between the atoms (the negative sign of the force indicates that it has the nature of a force of attraction). As regards its absolute value, this force grows with diminishing $r$ until a certain distance $r_1$ is reached. After this, the force decreases, and at a distance of $r_0$ between the atoms it becomes equal to zero. Upon a further reduction of $r$, a force again appears, but now as a force of *repulsion* that rapidly grows with a diminishing distance between the atoms and tends to infinity when $r \to 0$.

This curve $F = f(r)$ corresponds to a similar curve showing how the potential energy $U$ of the interaction of atoms depends on $r$ and is depicted in Fig. 153. The similarity of these curves should not surprise the reader because $F$ and $U$ are known to be related by the equation

$$F = -\frac{dU}{dr}$$

At a distance between the atoms equal to $r_0$ when the force of interaction equals zero, the potential energy passes through a minimum. An atom in

this position is customarily characterized by saying that it is at the bottom of a "potential well". This is obviously a position of equilibrium. We know that the equilibrium of a particle is characterized exactly by the sum of the forces applied to it being equal to zero and the potential energy being minimum.

## 9.2. CRYSTAL LATTICE

In crystals, the atoms or other particles forming them (ions, molecules), as we have already noted, are arranged in a regular order. One of the important consequences of such an order in the arrangement of the atoms is the difference in the properties of a crystal in different directions, or, as such a difference in properties is generally called, *anisotropy*.

Regularly arranged atoms inevitably have different densities in different directions. This can be clearly seen in Fig. 154 showing a possible arrangement of atoms in a crystal (the symbols used in this figure will be described below, on p. 403). We must only imagine that the atoms are arranged similarly outside of the plane of the drawing, forming a *space lattice* at whose *points* (or *sites*) the atoms are. If we draw planes through the lattice points in different directions (these are straight lines in our drawing), we shall see that the density of the atoms is different in these planes. A crystal, therefore, has planes "populated" differently with atoms. This is the main explanation of the anisotropy of crystals — their most characteristic property.

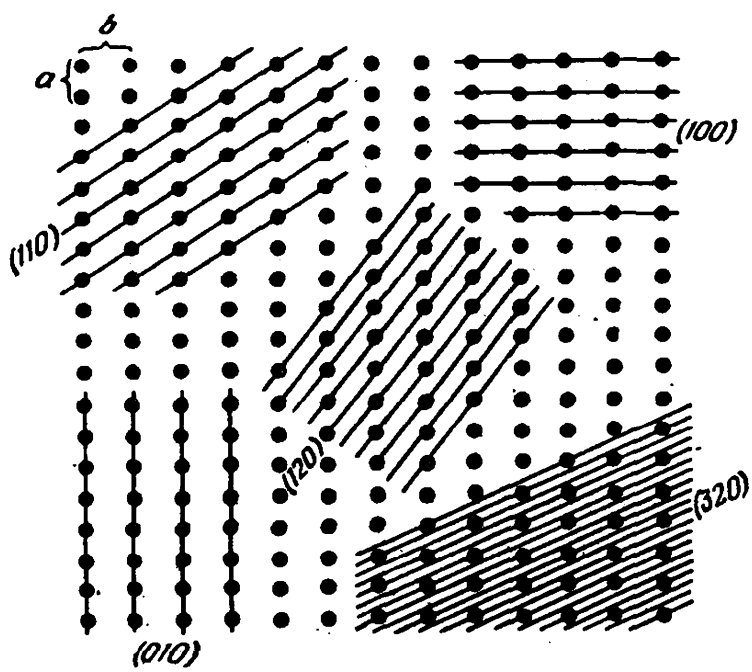



Fig. 154

Anisotropy manifests itself, for example, in that when a crystal is formed in conditions such that no external factors affect its growth, it takes on a definite shape with facetting characteristic of the given crystal. The crystal

is restricted by plane facets forming angles with one another that are also characteristic only of a given species of crystals. These facets are exactly the planes in which the particles are arranged with the greatest density so that upon growth of a crystal new atoms become attached to these planes in the majority of cases, and not to others. It is natural that in the most densely filled planes the atoms are bound to one another with the greatest force because here the distances between them are relatively smaller.

On the other hand, examination of Fig. 154 shows that the densely filled planes are relatively farther from one another than the less densely "populated" ones. Hence, the atoms in the densely filled planes are strongly bound to one another, but the force of interaction between such planes is not great, and they are comparatively easily separated from one another. As a result upon the mechanical destruction of a crystal, it can always be seen to split along certain definite planes, the so-called *cleavage planes*. A crystal of rock salt, for example, splits into pieces having the shape of rectangular parallelepipeds. The fragments of a crystal of Iceland spar have the shape of parallelepipeds, but not rectangular ones; mica and graphite split up into thin plates, etc.

It may be considered that the cleavage planes of crystals are exactly the planes containing the greatest number of atoms. The existence of cleavage planes is one of the characteristic features of crystals. When the conditions of growth of a crystal do not permit regular facets to be formed on it and its shape is therefore arbitrary, it retains all the other features of a crystal, particularly cleavage.

**Geometry of a Crystal Lattice.** A feature of a crystal, as we have already indicated, is the geometrically regular arrangement of the particles (atoms, ions, molecules). A crystal, consequently, has an intermittent periodic structure. From the geometrical viewpoint, such a periodically repeating arrangement of the particles can be achieved by means of an operation of parallel displacement called *translation*.

Suppose that we are moving point $p_0$ (Fig. 155) (let this point be, for instance, the centre of gravity of a particle) along a straight line over the distance $a$ to position $p_1$, next over the same distance to position $p_2$, etc.

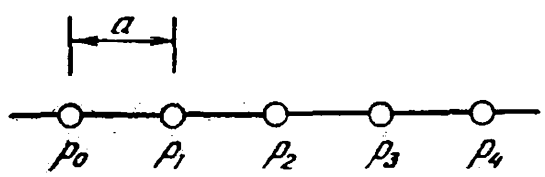



Fig. 155

Translation $\boldsymbol{a}$ thus gives us a number of points or a unidimensional chain of points. Translation $\boldsymbol{a}$ can be represented by a vector having a definite direction and a numerical value equal to $a$ called the *translation period*.

It is clear that the translation vector $\boldsymbol{a}$ can be used to represent an infinite multitude of parallel displacements — $2\boldsymbol{a}$, $3\boldsymbol{a}$, etc., in the general case $m\boldsymbol{a}$ translations, of which $\boldsymbol{a}$ is the smallest.

If we simultaneously subject point $p_0$ to the action of two operations of translation $\boldsymbol{a}$ and $\boldsymbol{b}$, as a result we get not a number of points, but a plane network (Fig. 156). The position of any point on this network is determined by the vector sum

$$m\boldsymbol{a} + n\boldsymbol{b}$$

where $m$ and $n$ are integers including zero.

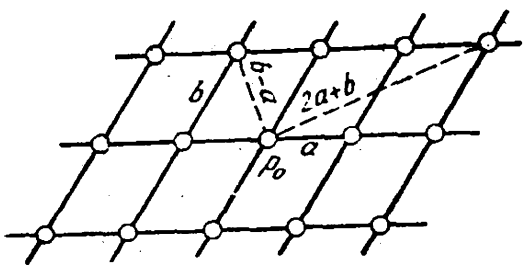



Fig. 156

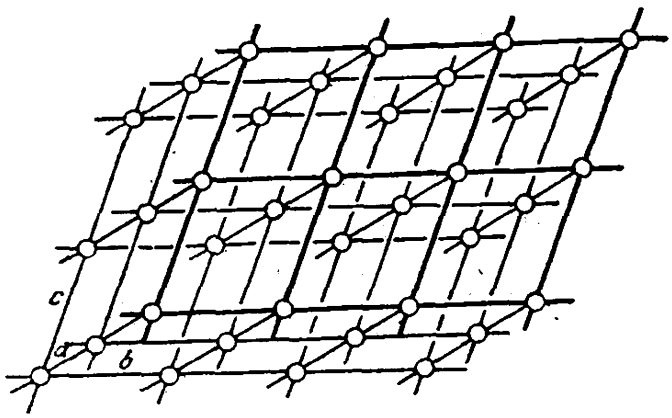



Fig. 157

If, finally, point $p_0$ is simultaneously subjected to three different translations $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, we get what is called a *space lattice*. The position of any point is determined in this case by the corresponding combination of displacements

$$m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$$

The combination of the three vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ is called a *translation group*. A parallelepiped formed by the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ is called an *elementary cell* (Fig. 157).

In every plane passing through any three points of a space lattice, the points (particles) are arranged in regular order forming a plane network. These are the crystal planes mentioned earlier. Some of them (the most densely "populated") are cleavage planes.

The translation vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ are the interatomic distances in the crystal lattice. Their numerical values are usually of the order of magnitude of $10^{-8}$ cm.

**Symmetry of Crystals. Elements of Symmetry.** Owing to the regular periodically repeating picture of the arrangement of atoms in a crystal, the latter has a definite *symmetry*.

The concept of symmetry is quite habitual in everyday life. Everyone is used to the fact that the human body is symmetrical, that a sphere is symmetrical, etc. What is the symmetry of a body characterized by? What, for example, does the symmetry of the human body consist in? The conventional answer that the symmetry of our body is determined by the circumstance that it consists of two identical parts — a right-hand and a left-hand ones—cannot be considered exact. For instance, our right and left

hands are not at all identical, we cannot put our right glove on our left hand and vice versa. Our two hands will become identical if one of them is reflected in a plane mirror. We could put the mirror reflection of our left glove onto our right hand! If we mentally draw a plane along our body through its middle and imagine that this plane produces a mirror reflection on both sides, then any point of one half (external) of our body when reflected from this plane will coincide with a similar point of the other half of our body. This mental mirror is called the *plane of symmetry* of a body. The symmetry of the human body consists in that if we reflect one half of a body from the plane of symmetry, it will coincide with the other half; it is customary to say that the plane of symmetry is an *element of symmetry* of the human body.

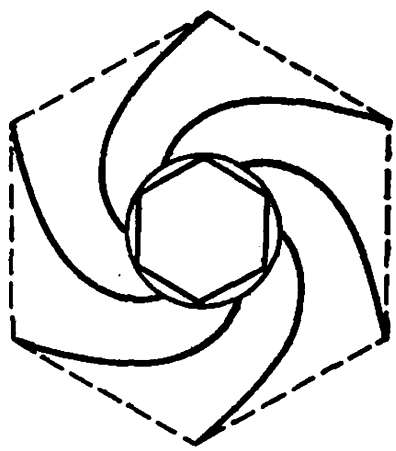


Fig. 158

The body shown in Fig. 158 is also symmetrical. Its symmetry consists in that it coincides with itself when rotated about an axis passing through its centre perpendicular to the plane of the drawing through an angle of 60 degrees. This axis is called the *axis of symmetry* of the body and is its *element of symmetry.*

Generally speaking, the property of symmetry of a crystal (or of any figure or body) consists in that as a result of certain mental operations the system of particles of the crystal (or in general of any system of points) coincides with itself, i.e. passes over to a position that does not differ from the initial one.

It is convenient to represent a symmetry of a crystal as a complex of separate elements of symmetry, with one of the operations just mentioned corresponding to each element. There are four such elements of symmetry for a crystal as a whole. They have the following names: axis of symmetry, plane of symmetry, centre of symmetry, and rotoflection axis of symmetry.

*Axis of Symmetry.* If a crystal has an *axis* (or, as it is sometimes called, a rotational axis) *of symmetry*, it can be made to coincide with itself, i.e. brought into a state not differing from the initial one by rotation through a certain angle about this axis.

Depending on the symmetry of the crystal, the magnitude of the angle of rotation needed for the crystal to coincide with itself may be 360, 180, 120, 90, and 60 degrees (i.e. $2\pi/n$, where $n = 1, 2, 3, 4$, or 6). Correspondingly, the axis of symmetry is called a one-fold, two-fold, three-fold, four-fold, or six-fold axis, or an axis of the first, second, etc. order. It can be shown from purely geometrical considerations that rotation about an axis through any other angle cannot make a crystal coincide with itself. This is why there cannot be a five-fold axis of symmetry corresponding to rotation through an angle of $360/5 = 72$ degrees or an $n$-fold axis, where $n$ is greater

than six. This is connected with the fact that when a system rotates for coincidence with itself it is essential that all the space be filled without leaving any empty spaces. It is known, however, that we can completely fill a space with regular triangles, parallelograms, hexagons, but we cannot do this with regular pentagons, heptagons, octagons, etc.

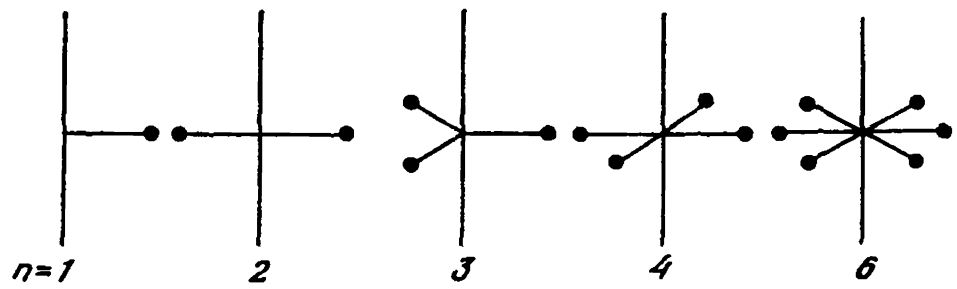



Fig. 159

Figure 159 shows all the possible axes of symmetry; the figures are the values of $n$.

The body shown in Fig. 158 evidently has a six-fold axis of symmetry. Rotation of the body through an angle of 360/6 = 60 degrees about an axis passing through its centre perpendicular to the plane of the drawing brings it into a position coinciding with the initial one.

*Plane of Symmetry.* If one half of a crystal coincides with the other one when reflected in a certain plane as in a mirror, such a plane is an element of symmetry of the crystal and is called its *plane of symmetry.* For the figure shown in Fig. 160, planes *1-1* and *2-2*, for example, are such elements: the parts of the figure at both sides of a plane are mirror images of each other.

But plane *3-3* also dividing this figure in half is not a plane of symmetry because reflection in this plane does not result in the two halves coinciding with each other.

*Centre of Symmetry.* If a crystal contains a point having the property that when the radius-vector $\mathbf{r}$ of any of the particles forming the crystal drawn from this point is replaced with the reverse vector $-\mathbf{r}$ the crystal passes over to a state that does not differ from the initial one, then this point, called the *centre of symmetry* (or the *centre of inversion)*, is an element of symmetry of the crystal.

*Rotoflection Axis.* The simultaneous application of two operations — rotation about an axis and mirror reflection in a plane perpendicular to the axis — leads to this element of symmetry. This means that a crystal has a *rotoflection axis of symmetry* if it can be made to coincide with itself by turning it through a certain angle about an axis (Fig. 161) and then reflecting it in a plane perpendicular to this axis. If the angle of rotation equals $2\pi/n$, then we have an $n$-fold rotoflection axis.

The symmetry of any crystal can be described with the aid of the four elements of symmetry listed above.

**Classes of Symmetry.** The above elements of symmetry may be combined in different ways in various crystals. In other words, various crystals may have several varying elements of symmetry. It is quite obvious that the

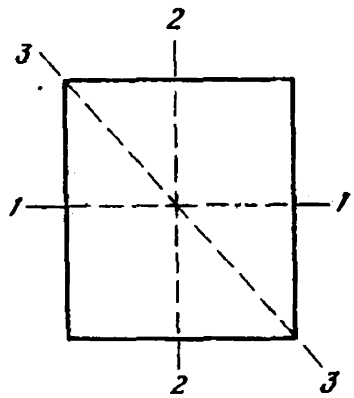


Fig. 160

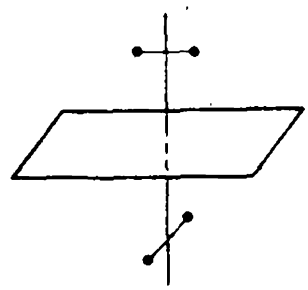


Fig. 161

greater the number of elements of symmetry which a given body has, the greater is its symmetry. A sphere, which has an infinite number of axes of symmetry, planes of symmetry, and a centre of symmetry, is the most symmetrical body.

Detailed consideration shows (this was done by A. Gadolin in 1867) that there are altogether 32 possible combinations of symmetry elements. Each of such possible combinations of symmetry elements is called a *class of symmetry.*

Only crystals belonging to one of the 32 symmetry classes can exist in nature, and this was confirmed experimentally. For example, crystals having only one axis of symmetry form five symmetry classes (of the 32) corresponding to the five orders of these axes including the first one when there is no symmetry. Four classes are formed by crystals having in addition to the axis of symmetry indicated above two-fold axes of symmetry perpendicular to it.

A separate symmetry class is formed by crystals having only a centre of symmetry, etc.

In crystallography, the above 32 symmetry classes are combined into *seven symmetry systems* that are named as follows in the order of growth of their symmetry:

the triclinic system combining two symmetry classes;
the monoclinic system including three classes;
the rhombic system also with three symmetry classes;
the trigonal system combining seven classes;
the hexagonal system with five classes;
the tetragonal system having seven classes;
the cubic system, the most symmetrical one, combining five classes.

**Bravais Lattice.** The symmetry elements and their classification given above related to crystalline bodies. These symmetry elements characterize the symmetry of a crystalline body as a whole; this is the so-called *macroscopic symmetry*.

Let us again return to the structure of a crystal lattice.

It was established above that a lattice can be made to coincide with itself (i.e. brought to a position that cannot be distinguished from the initial one) by translation, i.e. by parallel transfer over definite distances in definite directions. Translation is the main symmetry element for a crystal lattice.

We have already noted that any lattice can be represented in the form of regularly arranged parallelepipeds — elementary cells. All the elementary cells forming a lattice are obviously identical in shape and in volume, and each of them contains an identical number of atoms. There are identical atoms or groups of atoms at all the apices of the elementary cells; all these apices are therefore equivalent to one another and are *lattice points*.

Each of these points, i.e. each apex of an elementary cell, can be made to coincide with any other by parallel transfer over one of the lattice periods. These points, however, are not the only ones in a lattice. A lattice may also have points that can be made to coincide with one another with the aid of symmetry elements that are a feature of the crystal as a whole, i.e. by rotations and reflections.

In other words, in a crystal lattice, parallel transfers may be combined with macroscopic symmetry elements. If, for example, a crystal has an axis of symmetry or a plane of symmetry, then by parallel transfer (translation) of them over a lattice period an infinite number of such axes parallel to one another appear and, correspondingly, of planes of symmetry.

In addition, the combination of translation and rotation about an axis coinciding with the direction of this translation results in a new symmetry element called the *screw axis*.

Similarly, if a lattice point can be made to coincide with another one by combining translation of this point and its reflection from a plane parallel to the direction of translation, the corresponding symmetry element appears called a *glide-reflection plane*. A complex of equivalent lattice points that can be made to coincide with one another only by *parallel translation* form a so-called *translation* or *Bravais lattice* of a crystal.

A Bravais lattice, consequently, is a parallelepiped constructed by parallel translation of a lattice point in three directions. Directions parallel to the axes of symmetry of a crystal or perpendicular to its planes of symmetry are chosen as the directions (axes of coordinates). In crystallography, these directions are usually selected as the crystallographic axes. In parallelepipeds constructed in this way, the equivalent points (atoms) can be positioned not only at the apices, but also at the centre of the faces, and at the centre of a diagonal plane.

In the first case, the Bravais lattice is called *face-centered*, and in the second *volume-centered*.

The ratio between the edge lengths $a$, $b$, and $c$ of a Bravais lattice and the angles between them may be different. Here the question arises: how many different kinds of Bravais lattices can exist?

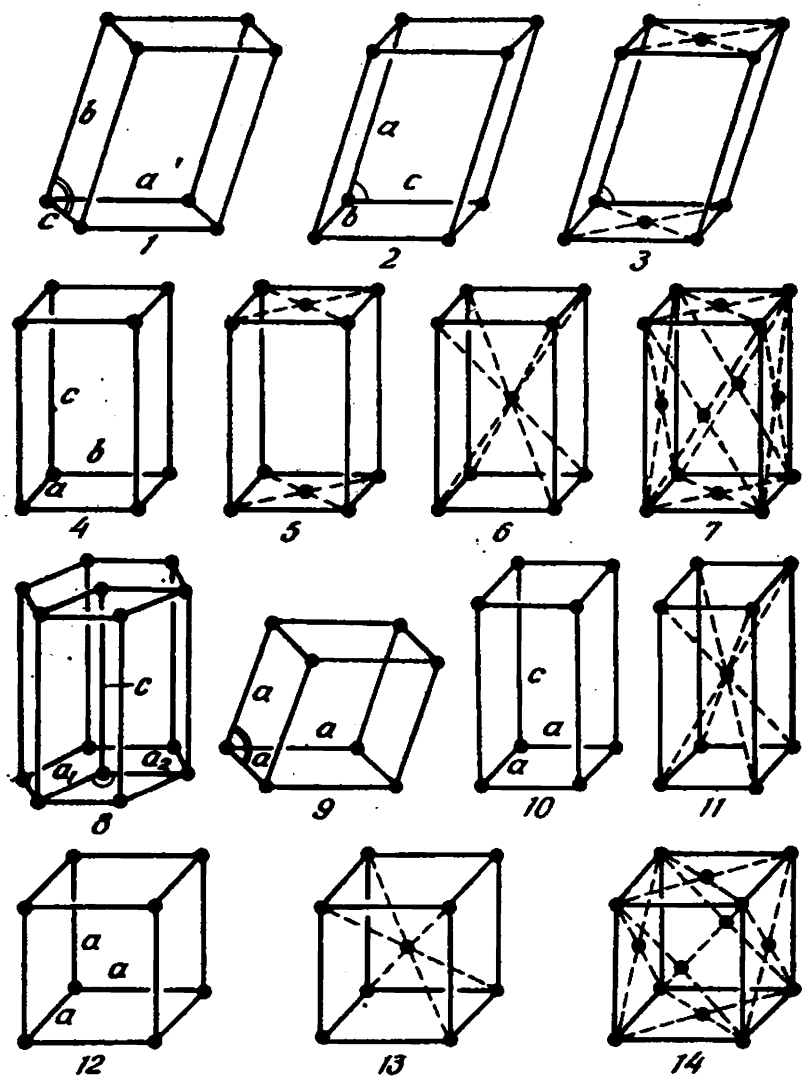



Fig. 162

It can be shown that there are altogether 14 different kinds of Bravais lattices. Since the crystallographic axes of a crystal are chosen as the coordinate axes on which these elementary parallelepipeds are constructed, then each Bravais lattice can be related to one of the seven crystal systems indicated above. Figure 162 gives all 14 elementary parallelepipeds of the Bravais lattices arranged in the order of growth of their symmetry. The first place has been given to the least symmetrical triclinic lattice *1* in which the points are at the apices of a parallelepiped with arbitrary edge lengths $a \neq b \neq c$ and with the angles between them $\alpha \neq \beta \neq \gamma \neq 90°$. Next come simple monoclinic lattice *2*, face-centered monoclinic *3*, simple rhombic *4*, rhombic with centered bases 5, rhombic volume-centered *6*, and rhombic face-centered lattice *7*. In hexagonal lattice *8*, the points are arranged at the apices of regular hexagonal prisms and at the centres of their

hexagonal bases. Further are Bravais rhombohedral lattice *9* whose elementary parallelepiped is a cube stretched or contracted along a space diagonal (rhombohedron), simple tetragonal *10*, and volume-centered tetragonal *11*. The cubic system, which has the maximum symmetry, includes three kinds of Bravais lattices: simple cubic *12*, volume-centered *13*, and face-centered *14*.

We have indicated above that the Bravais lattice is constructed for a quite definite point of a crystal lattice by its parallel translation along three crystallographic axes. If we choose a different point (atom) as the initial one, we get a different Bravais lattice. Hence it follows that there may be crystal lattices consisting of a system of several Bravais lattices displaced with respect to one another. For example, the crystal lattice of sodium chloride NaCl consists of two Bravais lattices (Fig. 163) in accordance with the fact that the $Na^+$ ions (black circles) and the $Cl^-$ ions (white circles) each separately form a cubic face-centered Bravais lattice. Both of these lattices are displaced relative to each other over half the edge of a cube.

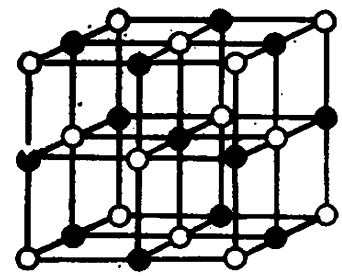


Fig. 163

**Space Groups.** The complete symmetry of a crystal lattice, i.e. the symmetry of the arrangement of the atoms forming it, is determined, as indicated above, by a combination of translational symmetry and symmetry elements connected with rotations and reflections. Such a combination results in the following symmetry elements: screw axes and glide-reflection planes. The combination of *all* the symmetry elements which a given crystal lattice possesses is called the *space group* of this lattice.

To determine the space group of a crystal lattice, it is necessary to indicate its Bravais lattice and those of its symmetry elements that are connected with rotations and reflections, i.e. the arrangement of the planes and axes of symmetry. Any space group can be related to one of the 32 crystal classes.

Detailed consideration shows that altogether 230 different space groups are possible, and these are distributed among the crystal classes indicated above. These 230 space groups were first discovered by the well-known crystallographer E. Fedorov.

**Symbols for Planes and Directions in a Crystal.** The anisotropy of a crystal makes it necessary to distinguish and designate in a definite way the different planes (faces) and directions (for example, edges) in a crystal. For this purpose, a special system of coordinates is used. It is related to a crystal so that the axes of coordinates are usually conducted parallel to axes of symmetry or at right angles to planes of symmetry, and the origin of coordinates coincides with one of the lattice points. The coordinates in such a system are measured in units equal to the interatomic distances in a given direction (these distances are called the *lattice constants* or *lattice parameters*). The position of a plane is unambiguously determined by

the coordinates of any three points in this plane, for example those at which it is intersected by the three axes of coordinates.

Suppose that axes *I*, *II*, and *III* are the coordinate axes and that we have to find the position of plane *S* (Fig. 164). If, for example, the plane intersects axis *I* at a point at a distances of four units from the origin of coordinates (i.e. at four interatomic distances in the direction of axis *I*), axis *II* at a distance of one unit, and axis *III* at a distance of two units from the origin of coordinates, then the position of the plane is given by the three numbers 4, 1, and 2.

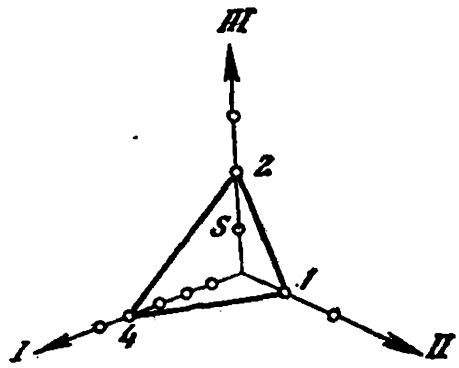


Fig. 164

It is customary practice, however, to use special *Miller indices* instead of these numbers to designate planes in a crystal. We determine the Miller indices as follows: we find the coordinates of the three points of intersection of the plane in question with the axes of coordinates (in units of the lattice constants). We reduce the reciprocals of the numbers obtained to a common denominator and discard the latter. The numerators of the fractions are the Miller indices.

For instance for the plane we have just considered which intersects the axes of coordinates at points 4, 1, and 2, the reciprocals of these coordinates will be 1/4, 1, and 1/2, respectively, the common denominator of these fractions is 4, and the Miller indices will thus equal 1, 4, and 2. These numbers are placed in parentheses so that the plane we are interested in is designated by the symbol (142) (which is read "one, four, two", and not "one hundred forty two").

The given set of indices obviously defines not one plane, but a whole family of parallel planes. The letter symbols used for the Miller indices are *h*, *k*, and *l*. If a plane is parallel to one of the axes of coordinates, i.e. intersects it at infinity, the corresponding index equals zero.

Figure 165 shows the indices of some of the most important planes of a cubic crystal.

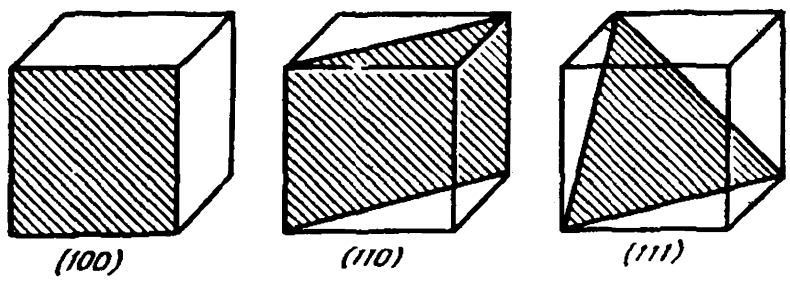


Fig. 165

*Directions* in a crystal are also set by indices that are determined as follows: a vector of an arbitrary length is taken along the direction being defined, and the values of the components of this vector along the axes

of coordinates are determined in units of the lattice constants. The three smallest integers whose ratios equal those of the vector components will be the indices of this direction. For example, if the components of a vector equal 6, 4, and 8 units, respectively, then the indices of the direction corresponding to this vector will be 3, 2, and 4. These numbers are written in brackets — [324]. The letter symbols used for the direction indices are $u$, $v$, and $w$.

A direction defined by a given set of indices $[u, v, w]$ is sometimes (and for a cubic crystal always) perpendicular to a plane having the same set of indices $(h, k, l)$.

## 9.3. DEFECTS IN CRYSTALS

In real crystals, we cannot observe the faultless order and strict periodicity in the arrangement of the atoms mentioned above. The most varied experiments point to the circumstance that the regularity in the arrangement of the atoms is generally violated to a certain extent.

First, it must be noted that although the atoms in a crystal lattice are arranged at such places which correspond to their equilibrium, this does not mean that they are at rest. The atoms in a solid, like those in a fluid, perform continuous thermal movements whose energy determines the temperature of the solid. We shall see below that these movements have the nature of small oscillations near the position of equilibrium, and the latter is a lattice point. Even if a crystal had a perfectly regular structure, the thermal movements of the atoms by themselves would violate the strict periodicity of the lattice. It is quite obvious that at each given moment part of the atoms are in the position of extreme deviation from the position of equilibrium, another part of them are in a position close to the middle one, a third part — in some intermediate position, and so on. And since the amplitude of the oscillations of the atoms even at moderate temperatures may reach several per cent of the interatomic distance, this leads to a noticeable violation of the periodicity of the lattice.

The degree of violation of the periodicity of a lattice changes with a change in the temperature.

Such thermal violations of the regularity of a lattice structure always exist, and they are a sort of background on which all the phenomena in crystals are staged. This is the reason why virtually all the properties of crystals depend in some way on the temperature. Only at absolute zero would a crystal be free of such violations of periodicity and be entirely ordered. A fully equilibrium state is possible only at absolute zero, but only if the crystal has no other violations of its structure or, as is said, has no *defects*.

There are also defects that do not result in thermal motion, but which almost always exist. However, they do usually appear because of this motion. Here we shall list some of the most important kinds of defects. All of them have a quite appreciable influence on the properties of crystals.

The first kind of defects called *Schottky defects* cons st in that some of the lattice points where atoms should be are vacant. It is natural that such "vacancies" cause the displacement of the neighbouring atoms relative to their normal position, and this leads to considerable violation of the regular structure of the lattice in the vicinity of a vacancy.

Another kind of defects called *Frenkel defects* appear when a particle leaves its place at a lattice point and takes up a position somewhere between the points (in the "interstice") surrounded by atoms occupying their "lawful" sites in the lattice. In this case, consequently, two defects are immediately formed (an interstitial-vacancy or Frenkel pair) because the vacant point and the atom in the interstice violate the regularity of the lattice to an equal extent.

Figure 166 shows schematically both kinds of the defects which we have just described.

The defects of the kinds described above, i.e. vacancies and atoms in interstices, are called *point defects*.

A third kind of defects in a crystal consists in that some of the points or sites in the lattice are occupied by foreign atoms forming a slight impurity in the main substance. Defects of this kind sometimes have a very great influence on the properties of the crystal. This relates especially to semiconductors whose properties are determined to a considerable extent by exactly such impurity defects.

If a crystal is formed by a substance that is a chemical compound corresponding to a definite chemical formula, defects may appear connected with there being a certain surplus or shortage of one of the components. In this case, the defects may have a varying nature: the surplus atoms, for example, may occupy positions in the interstices, they may behave like impurity atoms, etc.

The so-called *dislocations* are a very important kind of defect in a crystal. The nature of this kind of defect can be seen by examining Fig. 167. The defect consists in that in one part of the crystal (in the figure —in the upper part above the horizontal dash line) there appears one atomic plane more than in the other part. The "extra" atomic plane is naturally a distortion of the lattice and, as can be seen from Fig. 167, the part of the crystal

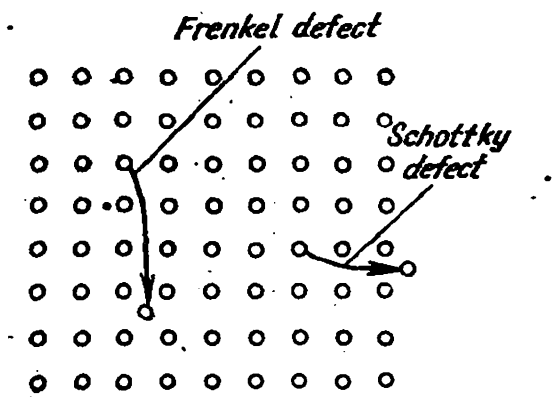



Fig. 166

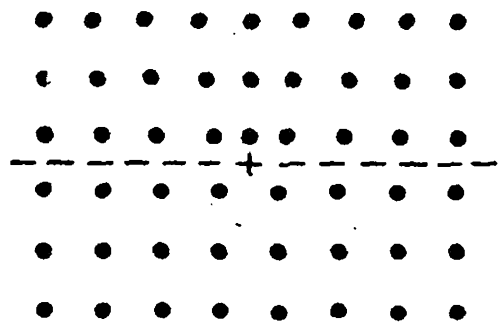


Fig. 167

directly adjoining the edge of the additional plane is distorted the most. The distortions gradually become smoothed out as the distance from this spot increases so that the region of great violation of the regularity of the crystal does not usually exceed several interatomic distances.

There is also another kind of dislocation called a *Burgers* or *screw dislocation*, which we shall not describe here. We shall only note that dislocations play an important part in crystals, especially in phenomena connected with the deformation of crystals because the presence of dislocations results in diminishing of their strength. The formation of dislocations also greatly affects the process of crystal growth (generally speaking, it facilitates this growth). The number of dislocations in crystals is quite great, and even in good natural crystals it reaches values of $10^8$ per cubic centimetre.

Dislocations are naturally not point defects but *linear* ones. The regularity of arrangement of the atoms is violated here along a *line* — the edge of the "surplus" atomic plane.

*Surface* (two-dimensional) defects also exist in crystals. They include, first, the surface of a crystal itself; second, the boundaries between separate parts of a crystal that are oriented somewhat differently — the so-called *mosaic blocks*; and, third, the boundaries between the crystallites in a polycrystal (the boundaries of the grains).

Finally, *volume* (three-dimensional) *defects* in the form of pores and cracks or fissures are also sometimes encountered in crystals.

**Equilibrium Concentration of Defects in a Crystal.** The points of a crystal lattice at which the atoms in the crystal are arranged are points where the potential energy of an atom is minimum. Therefore, a crystal absolutely deprived of defects ought to be in a state of stable equilibrium. Conversely, any defect in a crystal should increase its energy and make it less stable, and in any defective crystal a process of spontaneous "correction" of the crystal ought to take place.

Actually, however, matters are different. Completely perfect crystals do not and cannot exist. Order in the arrangement of the atoms is inevitably attended by a known degree of disorder that not only does not hinder the crystal from being in a state of equilibrium, but makes such equilibrium possible. The matter is that the atoms at the points of a crystal lattice, as indicated above, perform chaotic movements having the nature of small oscillations. The energy of these oscillations determines the temperature of the crystal so that this energy is of the order of magnitude of $kT$. Since the atoms interact with one another, the atomic oscillations are similar to the oscillations of connected pendulums. In such conditions, according to the laws of chance, fluctuational redistribution of the energy between the oscillating atoms is not only possible, but is inevitable. The result is that separate atoms receive energy considerably greater than $kT$, i.e. an energy that may be sufficient for an atom to be able to leave its "own" point of the lattice.

It may pass over to an interstice (a Frenkel defect), leave the crystal (a Schottky defect), join a dislocation, or move away to the surface of a fissure or pore. No matter what the "fate" is of an atom that leaves its place in a lattice, a *vacancy* is always formed. Part of the vacancies formed in this way disappear as a result of atoms getting into them from the interstices, dislocations, etc. The appearance and vanishing of the vacancies in the long run result in the setting in of equilibrium like that which sets in upon the evaporation and condensation of atoms over a liquid. The equilibrium concentration of the vacancies is determined as always in such cases by the Boltzmann equation [see Eq. (1.43)]

$$\frac{n}{n_0} = \exp\left(-\frac{E_v}{kT}\right) \tag{9.1}$$

where $n_0$ = number of molecules per unit volume of a crystal
$n$ = number of atoms which as a result of fluctuations have the energy $E_v$, i.e. an energy sufficient for an atom to leave its lattice point (the energy of formation of a vacancy).

Equation (9.1) permits us to assess the relative concentration of vacancies at various temperatures. For example at $T = 1000$ K, the ratio $n/n_0$ is close to $10^{-5}$: there is one vacant point for each hundred thousand atoms occupying their "lawful" points in the lattice.

The concentration of atoms in the interstices is much smaller because far from every atom that leaves a lattice point and thus creates a vacancy gets into an interstice.

## 9.4. MECHANICAL PROPERTIES OF SOLIDS. STRAINS

By the mechanical properties of solids are meant such properties that determine their ability to change their shape (deform) under the action o external mechanical forces and withstand destruction by these forces.

The deformation or strain of a solid is a result of an external force causing a change in the mutual arrangement of the particles which the solid consists of and in the distances between them.

A strain is called *elastic* if it vanishes after the action of the force causing it has stopped, and *plastic* if it remains after the action of the force has stopped. All solids can be strained both elastically and plastically depending on the magnitude of the applied forces. At sufficiently low forces, solids are strained elastically. It is quite obvious that in the components of various structures, machines, etc. intended for continuous service only elastic strains are permitted.

**Elastic Strain.** When external forces are applied to a solid and these forces are such that different parts of the solid body perform different movements, then the particles in a crystal are displaced relative to one another. This is exactly what the phenomenon of the *strain (deformation)* of a body consists in. Since here the mutual arrangement of the particles

and the distances between them change, this results in a change in the shape of the body, in its volume, or in a change in both. It must be noted in passing that deformation connected with a change in volume is possible not only in solids, but also in fluids: expansion and compression are deformations with a change in volume.

The changes in the mutual arrangement of the particles and the distances between them cause the appearance of *elastic forces* directed so that they tend, as it were, to restore the initial shape and volume and, consequently, the initial configuration of the particles. These forces act both within the body being strained, between its particles, and on other bodies in contact with them. These forces are directed opposite to the external forces causing movement of the particles, and if a body as a whole, notwithstanding the action of an external force, is not accelerated, then the elastic forces are balanced by the external forces, called a load. In this case, the strains are called *static*. They will be considered in the present section.

The relationship between the magnitude of the strain and the forces that appear because of it (or, which is the same, the external forces which they are equal to in absolute value) is determined by *Hooke's law*, which can concisely be expressed as follows: *the force is proportional to the strain*. To express this law quantitatively, we must agree on the quantities to be used for characterizing the strains and the forces.

Experiments show that if we separate a certain arbitrary surface in a deformed body, the strain determines not the force acting on this surface, but the ratio of this force to the surface area. This ratio equal to $F/A$, where $F$ is the force and $A$ the surface area, is called the *stress* ($p$). It is measured in the same units as pressure. By the word "force" in Hooke's law, we shall understand the stress. It should be noted that here we shall limit ourselves to a consideration of the strains of isotropic bodies.

If we designate the quantity characterizing strain by the Greek letter $\varepsilon$ (these quantities will differ for different kinds of deformation), then Hooke's law can be written in the form

$$\frac{p}{\varepsilon} = \text{const} \tag{9.2}$$

The constant equal to the ratio of the stress to the strain is called the *modulus* of the relevant kind of elastic deformation (this term was introduced by T. Young who gave Hooke's law a mathematical form).

The strains which a solid may experience under the action of an applied load can be divided into two main kinds in accordance with the fact that any force applied to the surface of a body can be resolved into two components, one perpendicular to the surface and the other parallel to it. The first of them causes a strain called *tension* or *compression*. This kind of strain is characterized by the fact that the volume of a body changes, but its shape remains unchanged. The second component (parallel to the sur-

face) causes *shear* strain. In the latter, the shape of a body changes, but its volume remains unchanged.

If the component of the stress parallel to the surface equals zero ($p = \sigma$, the normal stress), the strain will be pure tension or compression. If the normal component of the stress equals zero ($p = \tau$, the shear stress), we have pure shear.

In addition to the main kinds of strain considered above, two other kinds of strain are often encountered and play a great part: *torsion (twisting)* and *bending*. The former consists in shear strain, and the latter in tension and compression.

## 9.5. TENSILE AND COMPRESSIVE STRAINS. SHEAR

**Uniaxial Tension and Compression.** Suppose that a cylindrical bar having the length $l$ and the cross-sectional area $A$ is subjected to the action of the force $F$ directed parallel to its axis as shown in Fig. 168. The action

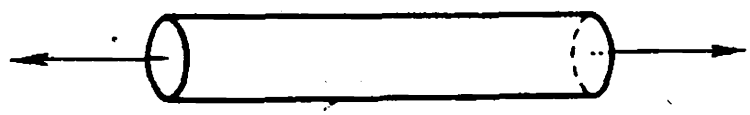


Fig. 168

of this force causes the length of the bar to increase by a certain amount $\Delta l$ (if we reverse the direction of the forces, the length will decrease instead of increasing). But this elongation $\Delta l$ cannot be taken as a characteristic of the strain. The force acts on each unit of length of the bar. Thus, the total elongation will depend on the length $l$ and will therefore be determined not only by the acting stress, but also by the original length of the specimen.

In the given case, the deformation should be characterized by the ratio of the elongation $\Delta l$ to the length $l$, which no longer depends on $l$. This ratio is called the *unit elongation* or the *tensile strain* of the bar and is designated by the Greek letter $\varepsilon$ ($\varepsilon = \Delta l/l$). Using such a characteristic of the deformation in uniaxial tension (compression denotes only a change in the sign of the strain upon a change in the direction of the force), we can write Hooke's law in the form

$$\frac{\sigma}{\varepsilon} = E$$

or

$$\varepsilon = \frac{\Delta l}{l} = \frac{\sigma}{E} \tag{9.3}$$

The quantity $E$ is called *Young's modulus* or the *modulus of elasticity* and is one of the main characteristics of the elastic properties of a solid. Its dimension coincides with that of pressure.

Sometimes Young's modulus is defined as the value of the stress that doubles the length of a specimen being stretched. This follows from the fact that if we introduce $\varepsilon = 1$ in Eq. (9.3), and this means that the length of the specimen has doubled, then $\sigma = E$.

Such a definition of Young's modulus is of an abstract nature because actually a linear relationship between the strain and the stress expressed by Eq. (9.3) is observed *only at low* strains ($\varepsilon \ll 1$). We cannot even speak of doubling of the length of a solid specimen because the latter will fail long before such a strain is reached! Moreover, long before a specimen fails, its strain stops changing linearly with the stress and, therefore, the very concept of Young's modulus loses its meaning.

Equation (9.3) can also be written in a different form:

$$\varepsilon = \alpha\sigma \tag{9.4}$$

where $\alpha = 1/E$.

The coefficient $\alpha$ equal to the reciprocal of Young's modulus is called the *coefficient of extension*. A glance at Eq. (9.4) shows that it numerically equals the unit elongation of a bar created by a stress equal to unity.

In uniaxial tension or compression, not only the length of a bar changes, but also its lateral dimensions, i.e. its radius: upon compression the radius grows, and upon tension it diminishes. If this deformation is also characterized by the relative change in the radius $\Delta r/r$, we can write

$$\frac{\sigma}{\Delta r/r} = M' \tag{9.5}$$

where $M'$ is a proportionality factor which can be called the *modulus of lateral compression in longitudinal tension*. It is quite obvious that there should be a simple relationship between $\varepsilon = \Delta l/l$ and $\Delta r/r$. It consists in that their ratio is a quantity that is constant for a given substance:

$$\frac{\Delta r/r}{\Delta l/l} = \mu \tag{9.6}$$

The constant $\mu$ equal to the ratio of the lateral and the longitudinal unit elongations is called *Poisson's ratio*. The value of this ratio obviously determines the change in the volume of a specimen being deformed.

If the volume of a body did not change in deformation, i.e. if the change in the length of a specimen $\Delta l$ were compensated by the corresponding change in the radius (for a cylindrical specimen), we would have

$$\mu = \frac{1}{2}$$

Indeed, the volume of a specimen is $V = \pi r^2 l$, where $r$ is the radius of the cylinder, and $l$ — its length. The change in the volume is

$$\Delta V = \pi(2lr\,\Delta r + r^2\,\Delta l) \tag{9.7}$$

For $\Delta V$ to equal 0, it is necessary that

$$2lr\,\Delta r = -r^2\,\Delta l$$

whence

$$\frac{\Delta r}{r} = -\frac{1}{2}\frac{\Delta l}{l}, \quad \text{i.e.} \quad |\mu| = \frac{\Delta r/r}{\Delta l/l} = \frac{1}{2}$$

Poisson's ratio for all substances is actually less than one-half and is close to 0.30, i.e. the volume of a body in linear deformation grows (Poisson's ratio for cork equals zero).

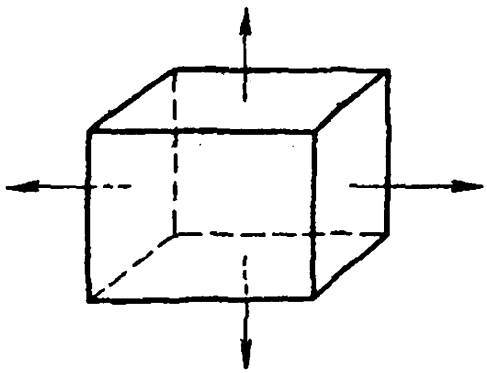


Fig. 169

**Uniform (Bulk) Tension and Compression.** This kind of deformation which in its nature does not differ from that considered above appears when the force acting on a body is distributed over its entire surface (Fig. 169).

Following the same considerations given above, we must take the relative change in the volume of the body, i.e. the quantity $\Delta V/V$, as the strain in the given case. In accordance with Hooke's law, we can therefore write

$$\frac{\sigma}{\Delta V/V} = M \tag{9.8}$$

The constant $M$ is the *bulk modulus*. Similar to Young's modulus, it is numerically equal to the stress that either doubles or halves the volume of a body.

Let us write Eq. (9.8) in the form

$$\frac{\Delta V}{V} = K\sigma \tag{9.9}$$

The coefficient $K$ equal to the reciprocal of the bulk modulus is called the *compressibility coefficient*. It is quite clear that this coefficient is very small for solids (of the order of magnitude of $10^{-6}$ atm$^{-1}$).

Uniform tension or compression can evidently be considered as a result of summation of three strains in uniaxial tension or compression (if they are small). Hence, the moduli $M$ and $E$ are related to each other in a simple way. It is easy to see that if Poisson's ratio equals zero, then $E = 3M$. Both moduli equal each other when $\mu = 1/3$.

**Shear.** This kind of deformation appears under the action of forces applied to two diagonally opposite faces of a body (Fig. 170). Such a system

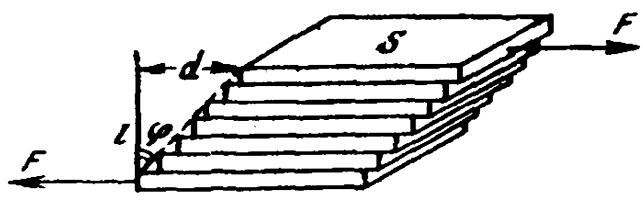



Fig. 170

of forces causes displacement of plane layers parallel to the direction of the forces relative to one another. A glance at the figure shows that the extreme layers become displaced over a certain distance $d$. If the original length of the specimen is $l$, then the strain can be characterized by the ratio $d/l$. Since at small values of $d$ this ratio equals $\varphi$, where $\varphi$ is the angle of shear of the planes, this angle is taken as a measure of the strain. Hooke's law can therefore be written in the form

$$\frac{\tau}{\varphi} = G \tag{9.10}$$

where $\tau$ is the shear stress. The constant $G$ is called the *shear modulus*. It is measured, like the other moduli of elastic strains, in pressure units.

The constant that is the reciprocal of the shear modulus is called the *coefficient of shear*. It numerically equals the angle of shear caused by a stress equal to unity whereas the shear modulus equals the stress causing shear through an angle equal to one radian.

We have already noted that shear strain is not attended by a change in the volume of the body being deformed.

## 9.6. RELATIONSHIP BETWEEN MODULI OF ELASTICITY

The moduli of elasticity and shear are naturally related to each other because they are characteristics, in essence, of one process — the rearrangement of the atoms in a lattice under the action of an external load. We shall find the relationships between the moduli of elasticity if we consider the general case of the action of arbitrary forces on a body.

Assume, for instance, that arbitrary forces are applied to a body having the shape of a cube. We can resolve each of them into its components acting along the three axes of coordinates. We shall denote the stresses directed along the axes $X$, $Y$, and $Z$ by $\sigma_x$, $\sigma_y$, and $\sigma_z$. Each of them induces the corresponding unit elongations (strains):

$$\left.\begin{aligned} \left(\frac{\Delta l}{l}\right)_x = \varepsilon_x, \quad \left(\frac{\Delta l}{l}\right)_y = \varepsilon_y, \quad \left(\frac{\Delta l}{l}\right)_z = \varepsilon_z \\ \varepsilon_x = \frac{\sigma_x}{E}, \quad \varepsilon_y = \frac{\sigma_y}{E}, \quad \varepsilon_z = \frac{\sigma_z}{E} \end{aligned}\right\} \tag{9.11}$$

It must be taken into account, however, that each elongation along an axis is accompanied by lateral compression along the other two axes. For example, the unit elongation $\varepsilon_x$ is accompanied by compressions along the $Y$-axis equal to $\mu\varepsilon_x$ and along the $Z$-axis also equal to $\mu\varepsilon_x$. In exactly the same way, the stress $\sigma_y$ induces not only the unit elongation $\varepsilon_y$, but also compressions $\mu\varepsilon_y$ along the axes $X$ and $Z$, while along the axes $X$ and $Y$ it induces the compressions $\mu\varepsilon_z$.

Hence, we must subtract the compression along the corresponding perpendicular axes from the expressions for the unit elongation $\varepsilon$. The equations for the unit elongations along the axes therefore become

$$\left.\begin{aligned} \varepsilon_x &= \frac{\sigma_x}{E} - \mu\varepsilon_z - \mu\varepsilon_y = \frac{\sigma_x - \mu(\sigma_z + \sigma_y)}{E} \\ \varepsilon_y &= \frac{\sigma_y}{E} - \mu\varepsilon_z - \mu\varepsilon_x = \frac{\sigma_y - \mu(\sigma_z + \sigma_x)}{E} \\ \varepsilon_z &= \frac{\sigma_z}{E} - \mu\varepsilon_x - \mu\varepsilon_y = \frac{\sigma_z - \mu(\sigma_x + \sigma_y)}{E} \end{aligned}\right\} \tag{9.12}$$

These expressions give the values of the strains along the axes $X$, $Y$, and $Z$.

Let us now assume that $\sigma_x = \sigma_y = \sigma_z$ (bulk compression). Hence, the expression for $\varepsilon_x$ will become

$$\varepsilon_x = \frac{\sigma - 2\mu\sigma}{E} = (1 - 2\mu)\frac{\sigma}{E} \tag{9.13}$$

The expressions for $\varepsilon_y$ and $\varepsilon_z$ are similar. Consequently in bulk compression the unit elongation along one of the axes equals $(1-2\mu)\,\sigma/E$ whereas in axial compression it equals $\sigma/E$ (along the direction of the stress).

From Eqs. (9.13) for $\varepsilon_x$, $\varepsilon_y$, and $\varepsilon_z$ it is easy to obtain an expression for the relative change in volume upon any strains, and the relationship between the bulk modulus and Young's modulus.

Suppose that a body having the form of a rectangular parallelepiped with edge lengths equal to $l_x$, $l_y$, and $l_z$ is subjected to deformation. Its volume obviously equals $V = l_x l_y l_z$. The action of the applied stresses $\sigma_x$, $\sigma_y$, and $\sigma_z$ will cause the volume of the body to change by the amount

$$\Delta V = \Delta(l_x l_y l_z) = l_y l_z\,\Delta l_x + l_z l_x\,\Delta l_y + l_x l_y\,\Delta l_z$$

The relative change in the volume in this case will be

$$\frac{\Delta V}{V} = \frac{\Delta l_x}{l_x} + \frac{\Delta l_y}{l_y} + \frac{\Delta l_z}{l_z}$$

Using Eq. (9.13), we find that in bulk (uniform) tension or compression, when $\sigma_x = \sigma_y = \sigma_z = \sigma$, the relative change in the volume is

$$\frac{\Delta V}{V} = \frac{3(1 - 2\mu)\sigma}{E}$$

But we know that

$$\frac{\sigma}{\Delta V/V} = M$$

consequently, the bulk modulus $M$ is related to Young's modulus $E$ by the equation

$$M = \frac{E}{3(1 - 2\mu)} \tag{9.14}$$

We know that shear strain is not attended by a change in volume. This means that

$$\frac{\Delta V}{V} = \varepsilon_x + \varepsilon_y + \varepsilon_z = 0$$

Substituting for $\varepsilon_x$, $\varepsilon_y$, and $\varepsilon_z$ in this expression their values from Eq. (9.12) yields

$$\frac{\Delta V}{V} = \frac{\sigma_x(1-2\mu) + \sigma_y(1-2\mu) + \sigma_z(1-2\mu)}{E} = 0$$

or

$$\sigma_x + \sigma_y + \sigma_z = 0$$

Only with such a selection of the stresses is shear strain possible. It follows from the latter equation that $\sigma_x = -(\sigma_y + \sigma_z)$. Using this expression for $\sigma_x$ in Eq. (9.12), we get

$$\varepsilon_x = \frac{\sigma_x + \mu\sigma_x}{E} = \frac{1+\mu}{E}\sigma_x \tag{9.15}$$

The quantity $\varepsilon_x = (\Delta l/l)_x$ is the ratio of the displacement of a face in shear to the length of this face. As can easily be seen, it equals half the angle of shear (upon small displacements) and characterizes the shear strain so that Eq. (9.15) can be written in the form

$$\frac{\varphi}{2} = \frac{1+\mu}{E}\sigma_x$$

or

$$G = \frac{\sigma_x}{\varphi} = \frac{E}{2(1+\mu)} \tag{9.16}$$

This equation is the one giving the relationship between the shear modulus, Young's modulus, and Poisson's ratio.

Table 19 gives the values of the moduli of elasticity for selected substances.

*Table 19*

| Substance | Young's modulus $E \times 10^{-10}$, N/m² | Shear modulus $G \times 10^{-10}$, N/m² | Poisson's ratio |
|---|---|---|---|
| Aluminium | 7.4 | 2.5 | 0.34 |
| Bronze | 12 | 4.4 | 0.38 |
| Copper | 12 | 4.4 | 0.34 |
| Lead | 1.6 | 0.6 | 0.44 |
| Nickel | 21 | 7.8 | 0.30 |
| Platinum | 17 | 6.3 | 0.39 |
| Quartz | 5.4 | 3.0 | — |
| Steel | 22 | 8.0 | 0.28 |
| Tungsten | 39 | 15.0 | — |

## 9.7. ELASTIC DEFORMATION AND THERMAL EXPANSION

The elastic properties of a solid must be related to thermal expansion because the latter in its nature is also a strain, although not induced by a mechanical load (see Sec. 9.21). The change in the dimensions and volume of a body as a result of thermal expansion or the action of an external stress is determined to an equal extent in the long run by the interatomic forces of interaction.

The relationship between the elastic properties and thermal expansion is based on the fact that the change in the volume upon tension or compression under the action of a load requires the performance of work equal, as we know, to the product of the pressure (stress) and the change in the volume. This work, in turn, equals the difference between the heat capacities at constant pressure and constant volume. It is precisely this quantity that can be expressed through the coefficient of thermal expansion and Young's modulus. Thermodynamic considerations lead to the following equation relating these quantities [see Eqs. (5.27) and (7.5)]:

$$C_p - C_V = TE\gamma^2 V \tag{9.17}$$

where $T$ = temperature
$E$ = Young's modulus
$\gamma$ = coefficient of volume thermal expansion
$V$ = molar volume of the substance.

Since for isotropic bodies we have $\gamma = 3\alpha$, where $\alpha$ is the coefficient of linear expansion, Eq. (9.17) can also be written in the following form:

$$C_p - C_V = 9\alpha^2 TEV \tag{9.18}$$

The shear modulus or coefficient does not enter this equation because shear strain is not attended by a change in volume.

Equations (9.17) and (9.18) can be used to calculate the values of $C_V$ if we know the heat capacity $C_p$, which can only be determined experimentally.

It should be noted that the difference $C_p - C_V$ for solids, as for fluids, equals the work done upon the expansion of one mole of a substance (if $C_p$ and $C_V$ are the molar heat capacities) as a result of heating by one kelvin. But for solids it naturally does not equal $R$ (as for ideal gases) because for solids the work done in their thermal expansion is mainly determined by molecular forces and not by the external pressure.

## 9.8. DEPENDENCE OF STRAIN ON STRESS

**Elastic Aftereffect.** The elastic deformations considered above are distinguished in that the strains strictly follow the stresses applied to a body, growing together with a growth in the stresses and vanishing together with them. Such strains, however, are observed far from always even at values of the stresses that do not yet cause plastic deformations.

We can sometimes observe that a body continues to deform after growth of the applied stress has stopped, and after removal of the stress the strain vanishes not immediately, but gradually. The strain, as it were, lags behind the stress inducing it: the body continues to deform after the stress stops growing, and after removal of the stress restores its original form only after a certain time, called the *relaxation time*. This phenomenon is called *elastic aftereffect (lag)*. The magnitude of the elastic aftereffect and the relaxation time depend on the temperature, and at sufficiently low temperatures the strain does not vanish at all after removal of the load, acquiring the nature of plastic deformation.

The elastic aftereffect is apparently connected with the imperfect nature of the structure of crystals (even monocrystals). A. Joffe showed that the elastic aftereffect is absent in perfect monocrystals.

**Plastic Deformation.** It was shown above that elastic deformation is characterized by its reversibility — the strain vanishes together with the disappearance of the deforming stress. This is exactly the strain for which Hooke's law holds, expressing the linear relationship between the stress and strain.

Experiments show that the deformation remains elastic, i.e. retains its reversibility, up to a quite definite value of the deforming stress for each substance. A further increase of the stress causes a more rapid growth of the strain than a linear one.

The maximum stress at which the deformation remains elastic is called the *elastic limit*. Figure 171 shows an experimentally obtained relationship between the stress $\sigma$ and the strain $\varepsilon$.

Elastic deformation obviously occurs up to the value of the stress equal to $\sigma_0$. At stresses exceeding this value, the straight line transforms into a curve. Hooke's law stops being true, and the deformation stops being elastic. If we increase the stress, for example, up to the value $\sigma_1$ at which the strain equals $OC'$ and then gradually reduce the stress to zero, the strain will also naturally diminish, but along straight line $BC$ instead of curve $BAO$. After the stress is completely removed, the body remains deformed by the value $OC$ *(permanent strain* or *set)*. The deformation is no longer reversible. Such deformation is called *plastic*.

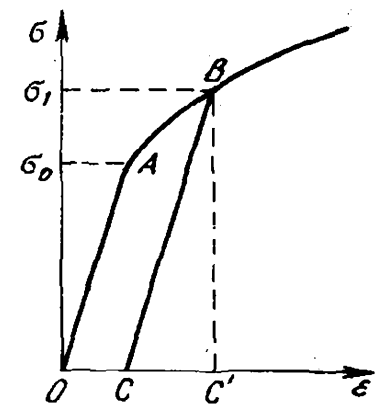


Fig. 171

In many solid bodies at stresses somewhat greater than the elastic limit, the strain *grows* at a *constant* value of the stress — it is customarily said that the material "yields". This value of the stress is called the *yield point*. In this case, the stress-strain relationship has the form shown in Fig. 172*c*. The horizontal section of the curve is called the yield line.

A further increase of the stress finally results in destruction of the body being deformed (in tension the result is rupture). The value of this stress is called the *ultimate strength* of the substance.

The shape of the curve $\sigma = f(\varepsilon)$ in the region preceding destruction may differ for different materials. Figure 172 shows some characteristic examples of such curves (destruction is shown on them by a cross). It can be seen

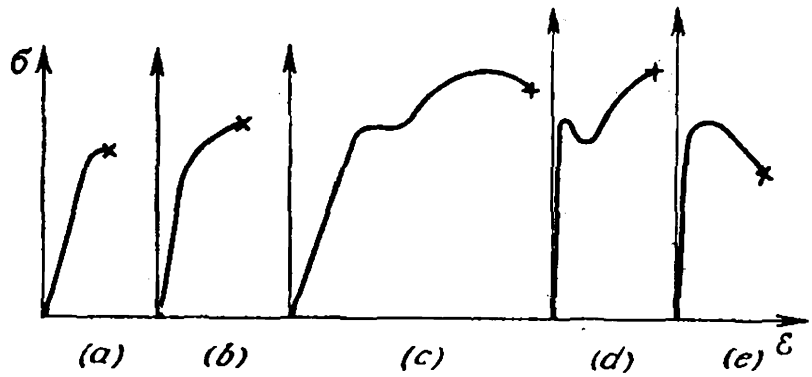



Fig. 172

from these curves that virtually no yield is observed for some substances (bronze, brass) (Fig. 172*b*). For other substances, the elastic limit and the ultimate strength are very close to each other. In such substances (cast iron, hardened steel), plastic deformation is virtually impossible — elastic deformation is directly terminated by destruction (Fig. 172*a*). Such substances are called *brittle*. The stress-strain curves sometimes have an unusual shape as in Fig. 172*d* and *e*.

The most interesting phenomenon connected with plastic deformation is observed upon the repeated loading of a body that has already (one or more times) undergone plastic deformation. Suppose that the body was subjected to deformation by the action of a stress exceeding the elastic limit, for example of a stress equal to $\sigma_1$ as shown in Fig. 171. After removal of the load, the body, as we saw, remains deformed with a permanent set equal to *OC* (see Fig. 171). If now this plastically deformed body is again subjected to the action of a stress, then with a growth of the latter the strain will again increase according to Hooke's law, even with the same value of Young's modulus (i.e. with the same slope of the straight line). But the elastic limit will now be higher than upon the first loading. The new elastic limit will approximately equal the maximum stress at which the first deformation was terminated. In Fig. 173 showing this repeated loading, the strain remaining after

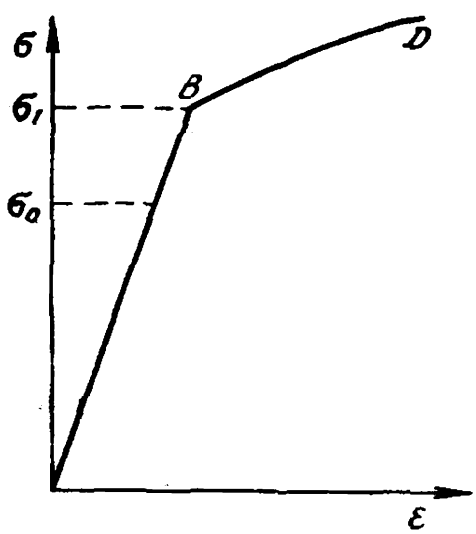



Fig. 173

the first loading is taken equal to zero. The elastic limit will now be $\sigma_1$ instead of $\sigma_0$. Portion *BD* of the curve in Fig. 173 is a continuation of section *AB* of the curve in Fig. 171.

Plastic deformation thus leads to an increase in the elastic limit of a material, i.e. to its hardening. This is widely used to harden metals and alloys in engineering.

The process in plastic deformation resulting in hardening of a material is called *work hardening* or *strain hardening*, and the state of a body hardened as a result of plastic deformation is called the strain hardened state.

**Heat Treatment.** The hardening setting in as a result of plastic deformation can be eliminated if the deformed body is subjected to long heating at a sufficiently high temperature. After such heat treatment, called *annealing*, the previous yield point is restored, and the residual stresses that may appear in a body if the deformation was not uniform are removed. The dimensions and shape of a body are not restored in annealing, however.

Another kind of heat treatment called *quenching* or *hardening* leads for some alloys, for example for steel, not to lowering but to elevation of the yield point, i.e. to hardening of the material. The body in this process is heated to a high temperature and then rapidly cooled, usually by immersion in water or oil.

In some cases (certain steels, alloys of non-ferrous metals), hardening is followed by another kind of heat treatment — second heating to a lower temperature than in hardening. This heat treatment is called *tempering* or *artificial ageing*.

The different kinds of heat treatment are widely used in the metal-working industry for improving the properties of metals and alloys.

It is interesting to note that hardening results in the improvement only of alloys. Pure metals do not take hardening, i.e. are not hardened as a result of such treatment.

We must note in this connection that pure metals as regards their mechanical properties in general differ very greatly from metals containing impurities and from alloys. These differences consist in that pure metals are very soft, have a low elastic limit, cannot be hardened, and in general have considerably poorer mechanical properties than alloys. This circumstance was known back in very ancient times; the first metal implements were made not from a pure metal (copper), but from an alloy of copper and tin — bronze, whose hardness and strength are considerably higher. The same should be said about bodies having a perfect crystalline structure: monocrystals have poorer mechanical properties than polycrystals of the same substance.

We shall see below what the reason is for this and many other features connected with plastic deformation.

## 9.9. MECHANISM OF PLASTIC DEFORMATION

Elastic deformation consists in that the application of external forces is attended by a slight displacement of the atoms from their normal equi-

librium positions. As a result, equilibrium is again restored in a crystal, this time between the forces of attraction and repulsion of the atoms on the one hand and the external forces on the other.

As regards plastic deformation, its mechanism and nature have meanwhile not been studied completely, although such phenomena as the hardening of plastically deformed bodies, heat treatment and the like have not only been known for a long time, but are being used for many thousands of years.

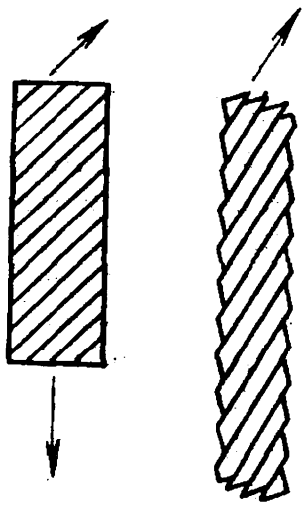


Fig. 174

We can consider it to be established, however, that unlike elastic deformation in which the atoms are only slightly displaced from their equilibrium position, in plastic deformation the separate layers of a crystal slip relative to one another (Fig. 174).

These slips along the atomic planes are not only "guilty" of shear strains, but in general of all kinds of deformation, not excluding tensile strains. This is indicated by the so-called *slip bands* observed in a microscope on the surface of plastically deformed monocrystals. These are the lines of intersection of the slip planes with the surface of the crystal.

In many cases, we can observe a change in the shape of the cross section of extended bars and roughness of their surface, i.e what should be expected if tension is attended by slipping of the crystal layers relative to one another. Slipping of the layers mainly occurs along the cleavage planes, which are populated the heaviest with atoms.

Thus, plastic deformation is connected with slipping, i.e. with shear of the crystal planes. For this purpose, it is obviously necessary that there are forces tangential to these planes. Such forces always exist when an external deforming load is applied. Indeed, no matter how the external force is directed, a crystal will always possess such slipping planes along which a component of this external force will act so that the possibility of shear exists even in tensile deformation.

Plastic yielding begins, as we know, only from a definite value of the stress (the yield point). This means that slipping along the crystal planes also begins from a quite definite critical value of the stress tangential to these planes. Naturally, this critical value of the stress (conventionally called the *shearing stress*) must not necessarily equal the elastic limit because only a certain component of the external stress acts along the planes. First slipping proceeds along that one of the crystal planes where the greatest component of the applied force is acting. Slipping begins along the other planes when the stress acting on them also becomes critical.

This is a general outline of the mechanism of plastic deformation. Since plastic yielding in the long run results in shifting of the atomic layers, we can approximately assess the stresses at which slipping should start

in a crystal and, consequently, plastic deformation, i.e. what the elastic limit of the crystal should be.

For this purpose, we shall consider the diagram of the process of slipping in an ideal crystal shown in Fig. 175. Figure 175*a* depicts an ideal crystal that has not yet been deformed. We must imagine the atoms to be arranged at the points of intersection of the lines and the crystal to extend in a direction at right angles to the plane of the drawing. The arrows show

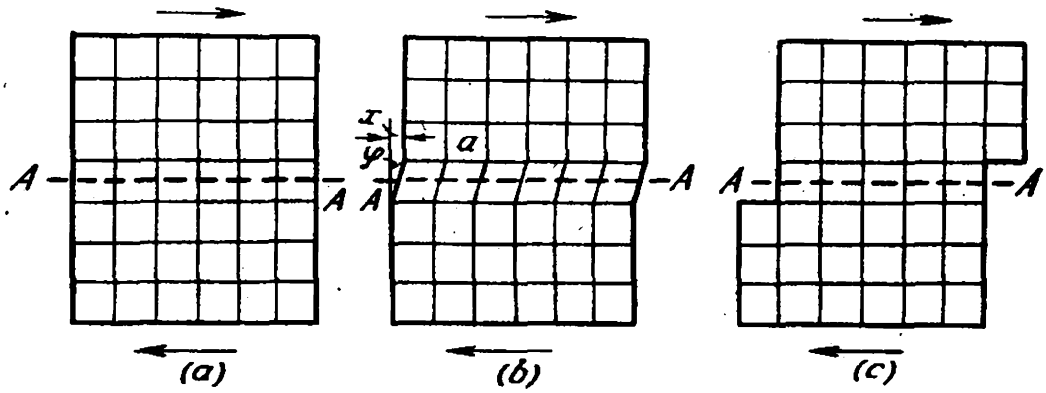



Fig. 175

the directions of the shearing stresses. Dash line *AA* denotes a slip plane. Before slipping begins (see Fig. 175*a*), the crystal is in equilibrium. When the action of the stresses causes one-half of the crystal to shift relative to the other over a distance equal to the lattice constant (see Fig. 175*c*), it will again be in equilibrium because the mutual arrangement of the atoms will be the same as at the beginning. In either of these positions, the shearing stress equals zero.

But it also equals zero when the atoms being displaced are in an intermediate position with symmetrical arrangement of the atoms relative to their neighbours. Hence it follows that the shearing force (stress $\tau$) is a periodical function of $x$ (see Fig. 175*b*) with a period equal to the lattice constant $a$. Adopting the simplest periodical function — a sinusoid, we can consider in the roughest approximation that

$$\tau = \tau_{\max} \sin \frac{2\pi x}{a} \tag{9.19}$$

If $\tau < \tau_{\max}$, then when the action of such a stress stops the atom will return to its initial position, and, consequently, no slipping will occur. It will only occur when $\tau = \tau_{\max}$. Hence, $\tau_{\max}$ is the critical shearing stress needed for slipping. It must be close in value to the elastic limit.

For small values of $x/a$, we may consider that $\sin 2\pi x/a = 2\pi x/a$. Therefore,

$$\tau = 2\pi\tau_{\max} \frac{x}{a}$$

But $x/a \approx \varphi$, where $\varphi$ is the angle of shear (see Fig. 175*b*). Hence,

$$\tau = 2\pi\varphi\tau_{max} \tag{9.20}$$

On the other hand, we know that in shear the ratio $\tau/\varphi$, i.e. the ratio of the stress to the angle of shear, equals the shear modulus $G$. Therefore,

$$G = 2\pi\tau_{max}$$

or

$$\tau_{max} = \frac{G}{2\pi} \tag{9.21}$$

The shear modulus, in turn, is numerically equal to the stress inducing a displacement through an angle of one radian. This means that as long as the stress is less than $G/2\pi$, no slip should occur and, consequently, there should be no plastic deformation (the equation $\tau/\varphi = G$ expresses Hooke's law).

It thus follows that at a stress equal to $G/2\pi$ the angle of shear will be about 1/6 radian, i.e. about 9.5°. If this angle is less, for instance 9°, then no plastic deformation will occur. Since plastic deformation corresponds to Fig. 175*c* (slipping has occurred) when the angle $\varphi = 90°$, this means that deformation is possible through about 15° without the appearance of yielding.

Experiments show, however, that plastic yielding in all monocrystals begins at strains that are hundreds and thousands of times less than that which we have just calculated. Even for polycrystalline bodies that are considerably stronger than monocrystals, plastic yielding begins at angles of shear equal to only tenths of a degree, and not to several degrees.

Thus, the theoretically calculated strength of crystals with respect to plastic deformation is many times greater than what is actually observed experimentally. The determination of the reasons for this discrepancy between theory and practice is one of the main problems facing the physics of plastic deformation.

In the following section, we shall treat a theory trying to explain this discrepancy and also other phenomena related to plastic deformation.

## 9.10. DISLOCATIONS IN CRYSTALS

The above calculations of the theoretical strength of a crystal with respect to shear are based on the assumption that we have to do with a perfect crystal in which the atoms are arranged with a faultless regularity. It is precisely such a crystal that should be distinguished by an unusually great strength, i.e. a high yield point (it should be remembered that plastic deformation in tension also consists in a multitude of displacements in small regions of a crystal). If experiments show that the yield point of a real crystal is actually much lower, it is natural to assume that the reason is

imperfection of the crystal and the presence of distortions in it, i.e. what we previously called defects.

On the other hand, however, crystals known to be defective often have a higher strength than crystals that are less distorted. There is no doubt, for instance, that the mechanical properties of steel, i.e. iron with an admixture of carbon, are higher than those of pure iron deprived of such defects

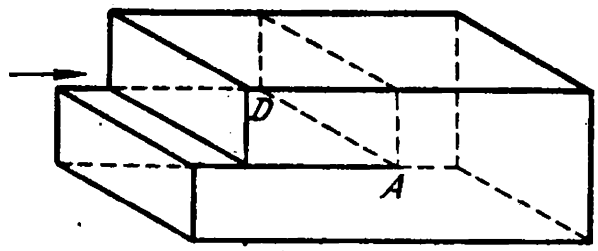



Fig. 176

as stranger atoms. In exactly the same way, a plastically deformed crystal is also a "spoiled", defective crystal, but its yield point is higher than that of a more perfect crystal that has not yet been subjected to strain hardening. Hence it follows that not any defects can be considered "guilty" of making the strength of a crystal less than the theoretically calculated one.

According to modern notions, many phenomena connected with plastic deformation can be explained by the presence of a special kind of crystal defects — dislocations, which we have already briefly described in Sec. 9.3. Let us now acquaint ourselves in greater detail with dislocations and their properties.

Imagine a crystal in which a notch has been made over half the depth of the crystal along a certain plane (Figs. 176 and 177). And now assume that the part of the crystal above the notch is compressed in the direction indicated by the arrow so that the extreme left-hand atomic plane is displaced over a distance equal to the lattice constant (see Fig. 176) while the lower part (under the notch) is not subjected to shear. Line *AD* inside the crystal is the edge of that part of it which was subjected to shear. The region of the crystal along this line is called an *edge dislocation*. Figure 178 shows the arrangement of the atoms in a plane at right angles to line *AD* (see Fig. 176). A glance at Fig. 178 shows that the defect — the dislocation —

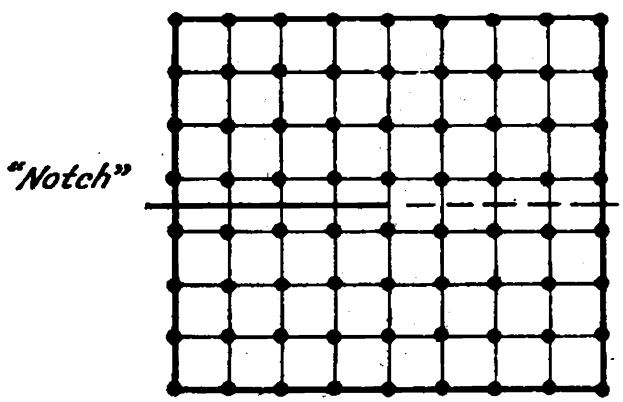



Fig. 177

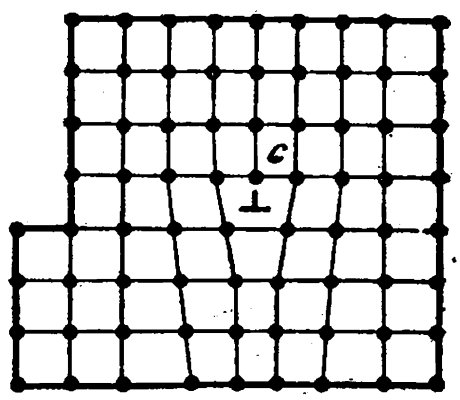



Fig. 178

consists in that atom *C* arranged directly on the dislocation line is deprived of the environment of neighbouring atoms that is normal for the atoms of a crystal.

We have depicted a dislocation here as the result of mentally unreal operations of "notching" and compression. Dislocations of the above kind can actually appear in a crystal by themselves as a result of non-uniform motion of the atoms in slipping just like the non-uniform movement of separate parts of a rug causes folds to appear in it. Dislocations may also be formed in the process of the growth of a crystal from a melt. We can therefore consider that dislocations exist in any crystal just like other defects also exist in it.

An important property of dislocations is their ability to move in the slip plane. If we imagine that the dislocation shown in Fig. 178 is travelling toward the right-hand edge of the crystal, then it is easy to see that when the dislocation reaches this edge the same will happen with the crystal as in the normal slip shown in Fig. 175, i.e. the entire upper half of the crystal will be displaced relative to the lower one over a distance equal to the lattice constant. It can be shown, however, that a considerably lower stress is needed for the shifting of a dislocation than for ordinary slipping. The same folds in the rug may serve as an analogy here — they are easier to remove by moving the folds themselves than by pulling the rug by its edge.

Even if there were only a single dislocation in a crystal, it would result in a multifold reduction of its yield point.

Thus, the discrepancy between the theoretically calculated and the experimentally measured values of the yield point of a crystal can be explained by the existence of dislocations in the crystal which in all other respects is quite perfect. The correctness of this explanation is apparently confirmed by experiments with monocrystals prepared in conditions excluding the appearance of dislocations. The yield point of monocrystals grown in this way was found to be very close to the theoretical value, i.e. very high.

Microscopic cracks on the surfaces of crystals facilitate the accumulation of dislocations in them. The cracks therefore lower the strength of the crystals. If we eliminate such cracks in some way or other, the strength of a crystal should grow. This was confirmed by an experiment performed by A. Joffe. He conducted the experiment with a crystal of rock salt submerged in water. Upon dissolving from its surface, the crystal almost completely lost all of its surface cracks, and the measured strength was considerably greater than upon measurements in ordinary conditions (the Joffe effect).

Our notion of dislocations also allows us to explain a number of other features relating to the mechanical properties of solids.

**Dislocations and Strain Hardening.** It is clear from the above that the strength of a crystal depends on how easy the dislocations travel. The lower the interference to the movement of the dislocations, the smaller should be the yield point of a crystal.

If, as always happens, a crystal has many dislocations instead of one, their interaction results in diminishing of the mobility of the dislocations. J. Franck and W. Read showed that the number of dislocations grows in the process of plastic deformation. The result is that the dislocations when travelling are forced to pass through one another, and since each dislocation is a place where order in the crystal is violated, such mutual penetration causes forces of repulsion and attraction to appear between them. Consequently, the mobility of the dislocations diminishes, and the crystal becomes stronger. This is the reason why crystals become stronger in plastic deformation.

**Dislocations and Impurities.** Impurities in a substance usually lead to a growth in strength and hardness. From the viewpoint of the theory of dislocations, this strengthening should also be a result of the lower mobility of the dislocations. The presence of impurities does result in the movement of the dislocations becoming more difficult.

From what has been said about dislocations (see Fig. 178), it is clear that the state of the atoms of a crystal at both sides of a dislocation, above and below the slip line, is different. The lattice is somewhat compressed above this line and stretched below it. As a result, the impurity atoms mainly gather in the vicinity of the dislocations: the atoms whose dimensions are less than those of the atoms of the basic lattice gather in the compressed part, i.e. above the slip line, while the bigger atoms gather under it in the stretched part. Such an accumulation of the impurity atoms near the dislocations results in the fact that a greater stress is needed for displacement of a dislocation. And this means that the body becomes stronger. Calculations show that a very small number of impurity atoms is needed (of the order of magnitude of 0.01% and less) for their accumulation at dislocations to result in strengthening. This explains the great influence of even very small impurities on the mechanical properties of solid bodies.

This also explains the fact that when an alloy is a mixture of two kinds of atoms of approximately identical dimensions (for example gold and silver), the strengthening is very small because in this case the impurity atoms "have no reason" to gather at the dislocations — at any other place of the lattice their energy will be approximately the same.

**Dislocations and Heat Treatment.** The removal of the consequences of strain hardening in annealing, like other cases of a change in the mechanical properties, is also connected with a change in the mobility of the dislocations.

In the given case, the mobility of the dislocations evidently grows because the yield point diminishes. This occurs for the following reason. At a high temperature, when the kinetic energy of the atoms increases, the impurity atoms gathering near the dislocations, at least partly, leave their places at the dislocations owing to diffusion, tending to level out their concentration throughout the entire volume of the body. The result is greater freedom of movement of the dislocations leading to lowering of the yield point — the latter tends to the value that existed before deformation.

The processes attending the other kinds of heat treatment (hardening, tempering) are somewhat more complicated because they are connected with the existence of different phases in alloys. The present book does not have consideration of these phenomena as its task. We shall only indicate that the theory of dislocations is very helpful when studying these processes too.

We shall add in conclusion to what has been said above about dislocations that there are many direct and indirect experimental proofs of their actual existence in crystals.

## 9.11. TRANSITION TO THE SOLID STATE

The establishment of ideal order in the arrangement of atoms, i.e. the formation of a solid, is prevented by thermal movements whose main feature, as we know, is their chaotic, disordered nature. Hence, for a substance to be able to be in the solid state, its temperature must be sufficiently low—so low that the energy $kT$ of the thermal movements will be less than the potential energy of interaction of the atoms.

A body can be an ideal (perfect) crystal in which all the atoms are in equilibrium and have the minimum energy only at absolute zero. All substances actually become solid at considerably higher temperatures. The only exception is helium which also remains liquid at absolute zero, but this is connected with certain quantum effects which will be briefly treated below.

A substance can pass into the solid state either from the liquid or the gaseous one. In both cases, such a transition is one from a state deprived of symmetry into a state in which symmetry exists (this relates at any rate to long-range order existing in crystals, but not existing in fluids). Therefore, the transition to the solid state must occur in a jump, i.e. at a definite temperature unlike the gas-liquid transition which, as we know, can also occur continuously.

Let us first consider the liquid-solid transition. The process of formation of a solid when a liquid cools is the process of formation of a crystal (crystallization), and it occurs at a definite temperature — the freezing or solidification point. Since the energy diminishes in such a transition, it is attended by the liberation of energy in the form of the latent heat of solidification. The reverse transition — melting — also occurs in a jump at the same temperature and is attended by the absorption of energy in the form of the latent heat of melting equal in magnitude to the heat of solidification.

This can be clearly seen from the graph of the time dependence of the temperature of a cooling liquid shown in Fig. 179 (curve *a*). Section *1* of curve *a* shows the course of the monotonous lowering of the temperature of the liquid owing to the removal of heat from it. Horizontal section *2* shows that at a definite value of the temperature its lowering stops, although the removal of heat continues. After a certain time, the temperature again begins to lower (section *3*). The temperature corresponding to section *2* is the solidification (freezing) point. The heat liberated in solidification

compensates for the removal of heat from the substance, and therefore lowering of the temperature temporarily stops. After completion of the solidification process, the temperature, now of the solid, again begins to lower.

Such a course of the graph of temperature lowering is characteristic of crystalline bodies. When liquids are cooled that do not form crystals

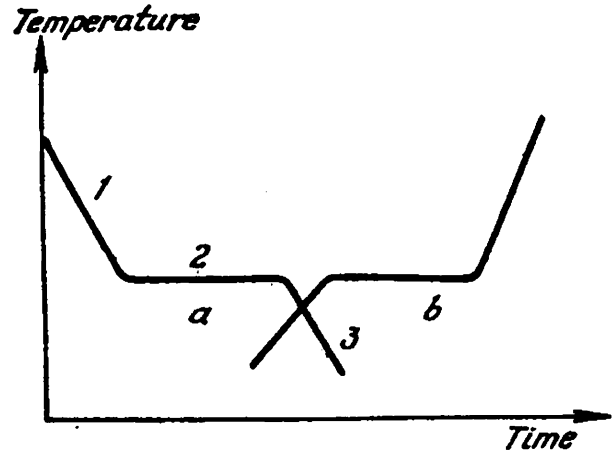



Fig. 179

(amorphous substances), no latent heat is liberated and the cooling graph is a monotonous curve without the *discontinuation* of cooling.

In the reverse process of the transition of a substance from the solid state to the liquid one (melting), a *stop* in elevation of the temperature is also observed on the heating curve owing to the absorption of the latent heat of melting — the heat at whose expense the crystal lattice is destroyed (curve *b* in Fig. 179).

For crystallization (solidification) to begin, one or more centres of crystallization must be present. The capacity of such centres could be filled by chance clusters of particles of the liquid adhering to one another which could be joined by new and new particles until the entire liquid transformed into a solid. The formation of such clusters in a liquid itself, however, is hindered by thermal movements which destroy them before they have time to acquire appreciable dimensions. Crystallization is noticeably facilitated if a liquid from the very beginning contains sufficiently large solid particles in the form of grains and bodies that become centres of crystallization.

The formation of centres of crystallization in a liquid itself is naturally facilitated with lowering of the temperature. Therefore, the crystallization of a pure liquid deprived of foreign inclusions usually begins at a temperature that is somewhat lower than the true solidification point. In ordinary conditions, a solidifying liquid has many centres of crystallization so that a multitude of tiny crystals are formed in the liquid which intergrow, and the solidified substance will be *polycrystalline*.

A single crystal — a *monocrystal* growing from a single centre of crystallization that is the only one in the liquid — can be obtained in special conditions which are usually hard to provide. If identical conditions of accumulation of the particles are ensured for all directions, the crystal obtained will be regularly faceted in accordance with its symmetry properties.

The liquid-solid transition like the reverse one is a phase transition because the liquid and solid states can be considered as two phases of a substance. Both phases at the freezing (melting) point can be in contact with each other, being in equilibrium (ice, for example, can float in water without melting), just like a liquid and its saturated vapour can be in equilibrium.

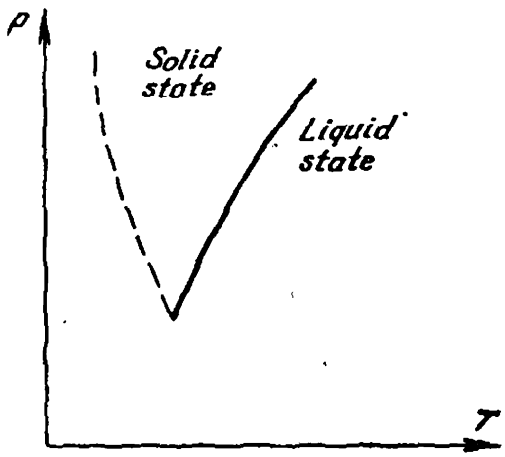


Fig. 180

*Similar to how the boiling point depends* on the pressure, the freezing point (and the melting point equal to it) also depends on the pressure, usually growing with the latter. It grows because the external pressure brings the atoms closer together, and to destroy the crystal lattice in melting the atoms must be moved apart: at a greater pressure a higher energy of the thermal movements is needed for this, i.e. a higher temperature.

Figure 180 shows a curve of the pressure dependence of the melting (freezing) point. The solid curve divides the entire $p$-$T$ region into two parts. The region to the left of the curve corresponds to the solid state, and the region to the right of it to the liquid state. Any point on the melting-point curve itself corresponds to equilibrium of the solid and liquid phases. At these pressures and temperatures, a substance in the liquid and solid states is in equilibrium, the two states being in contact with each other. The liquid does not solidify, and the solid does not melt.

*The dash curve in Fig. 180 is a melting-point curve for the few substances* (bismuth, antimony, ice, germanium) in which the volume increases instead of diminishing in solidification. For such substances, the melting point naturally lowers with increasing pressure.

The change in the melting point $dT$ is related to the change in the pressure $dp$ by the Clapeyron-Clausius equation [see Eq. (7.62)]

$$\frac{dT}{dp} = \frac{T(V_2 - V_1)}{L}$$

where $T$ = melting (freezing) point
$V_1$ and $V_2$ = molar volumes of the liquid and solid phases, respectively
$L$ = molar heat of fusion.

This equation also holds for other phase transitions. Particularly, for evaporation and condensation, the Clapeyron-Clausius equation was derived in Chap. 7 [see Eq. (7.58)].

Inspection of the Clapeyron-Clausius equation shows that the sign of the change in the melting point with a change in the pressure is determined by which of the two quantities $V_1$ and $V_2$ is greater. The steepness of the curve also depends on the value of the latent heat of transformation $L$: the smaller the value of $L$, the less does the melting point change with the pressure. Table 20 gives the values of the specific (i.e. related to a unit mass) heat of fusion for selected substances.

*Table 20*

**Specific Heat of Fusion for Selected Substances**

| Substance | Specific heat of fusion $L \times 10^{-5}$, J/kg | Substance | Specific heat of fusion $L \times 10^{-5}$, J/kg |
|---|---|---|---|
| Aluminium | 3.94 | Mercury | 0.11 |
| Copper | 1.71 | Silver | 1.05 |
| Gold | 0.66 | Sodium chloride | 5.19 |
| Lead | 0.23 | Water (ice) | 3.32 |

The Clapeyron-Clausius equation can also be written in the following form:

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$

This equation shows how a change in the temperature affects the pressure at which the two equilibrium phases are.

A solid can be formed not only by the crystallization of a liquid, but also by the condensation of a gas (vapour) into a crystal without passing through the liquid phase. Here also the latent heat of transformation is liberated which, however, is always greater than the latent heat of fusion. The formation of a solid at a definite temperature and a definite pressure can occur either directly from the gaseous state or by preliminary liquefaction. In both cases, the initial and final states are the same. Hence, the difference between the energies of these states is also the same. But in the second case, the latent heat of condensation is first liberated upon the transition from the gaseous to the liquid state, and then the latent heat of freezing upon the transition from the liquid to the solid state. It thus follows that the latent heat upon the direct formation of a solid from the gaseous phase should equal the sum of the heats of condensation and of freezing of the liquid. This relates only to heats measured at the melting point. At lower temperatures, the heat of condensation of a gas grows.

The reverse process of evaporation of a solid is generally called *sublimation*. The evaporating particles of the solid form a vapour over it in

exactly the same way as in the evaporation of a liquid. At definite values of the pressure and temperature, a vapour and a solid can be in equilibrium. A vapour that is in equilibrium with a solid is also called *saturated*. As for a liquid, the pressure of the saturated vapour over a solid depends on the temperature and rapidly diminishes with lowering of the temperature. Hence, the saturated vapour pressure of many solids is negligible at ordinary temperatures.

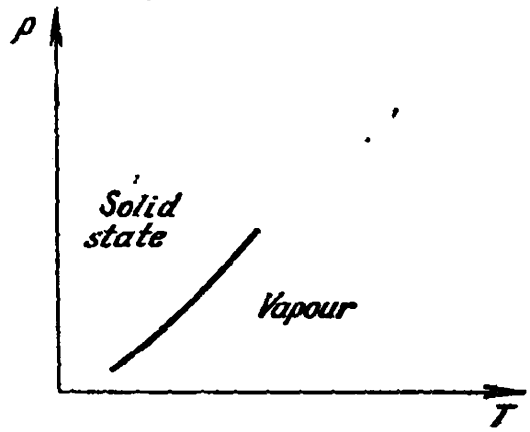


Fig. 181

Figure 181 shows the shape of the curve giving the temperature dependence of the saturated vapour pressure. This curve is the line of equilibrium between the solid and gaseous phases. The region to the left of the curve corresponds to the solid state, and to the right of it to the gaseous state. Sublimation, like melting, is connected with destructions of the lattice and requires the expenditure of the energy needed for this purpose. This energy manifests itself as the latent heat of sublimation equal to the latent heat of condensation. The heat of sublimation is therefore equal to the sum of the heats of fusion and vaporization.

## 9.12. PHASE DIAGRAM. TRIPLE POINT

Let us now depict melting-point and sublimation curves on the same graph in the coordinates $p$ versus $T$. Examination of Fig. 182 shows that both these curves having a different steepness (owing to the different values of the latent heats of fusion and of sublimation) intersect at a certain point corresponding to a definite pressure $p$ and temperature $T$. We know that melting-point curve *2* is a curve of equilibrium between the solid and liquid phases. In exactly the same way, sublimation curve *1* is a curve of equilibrium between the solid and gaseous phases. Hence, to the left of curves *1* and *2* there is a region of pressures and temperatures at which the solid state of the substance is the stable one. To the right of these curves are the regions of the liquid and gaseous states.

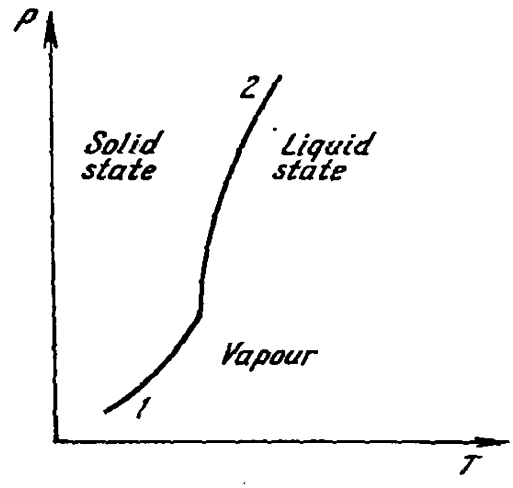


Fig. 182

The liquid and gaseous phases, in turn, are separated in the $p$-$T$ diagram by the vaporization curve, i.e. a curve along which the liquid and the vapour are in equilibrium. Since the heat of vaporization differs without fail from the heats of sublimation and of fusion, the

vaporization curve should intersect the melting-point and sublimation curves. If we were to show in Fig. 182 the vaporization curve too, it would intersect the melting-point and sublimation curves at a certain point with the coordinates $p_t$ and $T_t$ (Fig. 183). The point of intersection of these three curves is the point of equilibrium of three phases of a substance — solid, liquid, and gaseous. Consequently, at the temperature $T_t$ and the pressure $p_t$, all three phases of a substance in contact with one another will be in equilibrium, i.e. the liquid will not evaporate and not crystallize, the solid will not melt, and the gas (vapour) will not condense. Such equilibrium of all three phases is impossible at any other pressure and temperature.

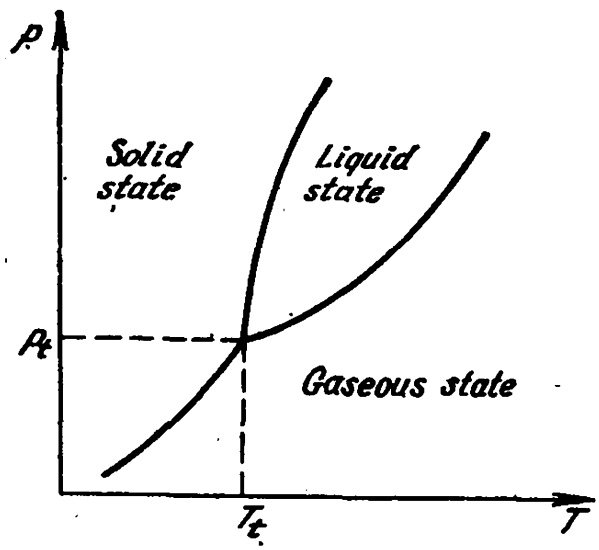



Fig. 183

The point of a *phase diagram* corresponding to equilibrium of all three phases of a substance is called the *triple point.*

The pressure $p_t$ and the temperature $T_t$ of the triple point differ for different substances. For example for water, $p_t = 4.6$ mm Hg and $T_t = 0.01$ °C. Table 21 gives the parameters of the triple point for selected substances.

*Table 21*

| Substance | Temperature at triple point, K | Pressure at triple point, atm |
|---|---|---|
| Carbon dioxide | 216.5 | 5.11 |
| Ammonia | 195.4 | $6\times10^{-2}$ |
| Water | 273.16 | $6\times10^{-3}$ |
| Ether | 152.9 | $8.5\times10^{-6}$ |

A glance at the phase diagram in Fig. 183 shows that a solid cannot always be transferred into the liquid state by heating. If we heat a body under a pressure less than $p_t$, it will not melt, but will directly pass into the gaseous state omitting the liquid phase — the substance will sublime instead of melting.

Melting, i.e. a transition to the liquid state, is possible only upon heating under a pressure exceeding $p_t$.

For many substances, the pressure corresponding to the triple point is less than one atmosphere. These substances melt when heated at atmospheric pressure. Substances also exist, however, for which $p_t$ exceeds 1 atm. They sublime instead of melting when heated at an ordinary pressure. For example for carbon dioxide ($CO_2$), the pressure $p_t$ is 5.1 atm and the temperature $T_t$ is minus 57 °C. Therefore at atmospheric pressure, solid carbon dioxide can exist only at a low temperature. It is in equilibrium with its vapour at atmospheric pressure at −80 °C. Solid carbon dioxide is used in this form. This is the widely used "dry ice", but this "ice" never melts — it only evaporates.

Two of the three equilibrium lines—the sublimation curve and the vaporization curve — have a beginning and an end. Namely, the sublimation curve begins at absolute zero and terminates at the triple point; the vaporization curve begins at the triple point and terminates at the critical point. As regards the melting-point curve, it also begins at the triple point, but has no end. At any rate, we know of no experiments which would show that the melting-point curve terminates "naturally" at any special point. On the contrary, experiments show that the melting point constantly grows with increasing pressure. For anomalous substances, i.e. such substances for which a growth in the pressure is attended by lowering of the melting point, the melting-point curve upon extrapolation intersects the pressure axis. This corresponds to the fact that at sufficiently great pressures a substance should melt at very low temperatures and may even remain liquid at absolute zero.

Experiments show, for example, that an increase in the pressure up to 180 000 atm results in lowering of the melting point of germanium from 986 to 276 °C.

We shall note in conclusion that no more than three phases can be in equilibrium in a substance consisting of a single component (the phase rule). Hence, if a substance of this kind has more than three different phases, there will also be more than one triple point, but only three equilibrium curves will converge at each of them. We encounter such a state of affairs, for example, when the same substance can have several crystalline modifications that are stable at different pressures and temperatures. The property of crystals to have different modifications is called *polymorphism*; the transition from one such modification to another is called a *polymorphic transition.*

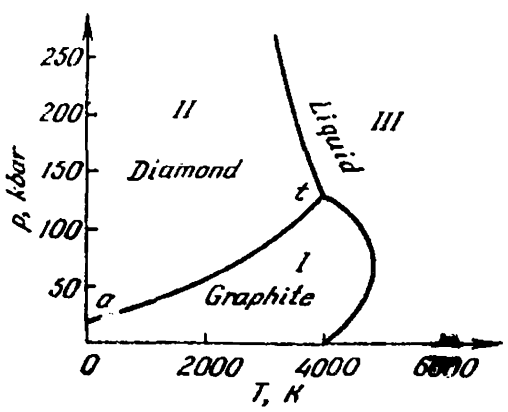


Fig. 184

An interesting and important example of a phase diagram for a substance with polymorphic transition is that for carbon, which is encountered in two crystalline modifications—graphite and diamond. The phase diagram has the form shown in Fig. 184. Here the triple point $t$ corre-

sponds not to equilibrium of the liquid, solid, and gaseous phases, but to the equilibrium of two solid phases (graphite and diamond) and the liquid phase. A pressure of 130 kbar (about 130 000 atm) and a temperature of 4000 K correspond to this triple point.

Region *I* in the diagram is the region of pressures and temperatures at which graphite is the stable modification of carbon, diamond is stable in region *II*, and liquid carbon in region *III*. Line *at* is the line of equilibrium of the two solid phases — diamond and graphite.

It follows from the diagram that at low pressures and temperatures graphite is the stable modification of carbon while diamond is stable at high pressures — not lower than 15 000 atm (the pressure corresponding to point *a*). This, however, does not mean that diamond cannot exist at the pressures and temperatures corresponding to region *I*. It is well known that diamond at ordinary pressures and temperatures not only exists, but also seems to be quite stable. But actually diamond in these conditions is *metastable*, i.e. is in a state of unstable equilibrium. Its "instability" is such, however, that it can exist in these conditions for an infinitely long time, and only when heated to a temperature above 1000 K does it begin to transform into stable graphite. In exactly the same way, graphite, which is unstable in region *II*, can actually also exist in this region, and also for an infinitely long time. This means that if by elevating the pressure and temperature we transfer graphite into region *II*, this will not necessarily result in its transforming into diamond.

Nevertheless, the alluring problem of converting abundant and cheap graphite into immeasurably more valuable diamond has not only been solved in the last 20 years, but a whole branch of industry has sprung up for the production of artificial diamonds. Graphite (or some other carbon-containing substance) is converted into diamond at pressures of about 60 to 100 thousand atmospheres and temperatures of 1500 to 2000 K, but without fail in the presence of catalysts. These are such metals as iron, tantalum, and nickel, and their part possibly consists in dissolving the graphite. At pressures of about 200 000 atmospheres and temperatures of about 3000 K, however, graphite transforms into diamond even without catalysts. It is important here that removal of the pressure and cooling, i.e. a return to region *I*, do not result in the reverse transformation of diamond into graphite.

Artificial diamonds are widely used in industry as the cutting part of various tools for processing articles.

Polymorphic transformation is also a phase transition. It is attended by the liberation (or absorption) of the latent heat of transition because rearrangement of the crystal lattice occurs in each such transition. It involves without fail a change in the energy of the particles in the crystal. When a substance undergoes polymorphic transformations, its melting-point curve may have a beginning and an end — it may begin at one triple point and terminate at another one.

## 9.13. PHASE TRANSITIONS OF THE FIRST AND SECOND KINDS

We have considered transitions from the liquid and gaseous states to the solid one, i.e. freezing or crystallization, and the reverse transitions — melting and sublimation. In Chap. 7, we acquainted ourselves with the transition of a liquid into a vapour — vaporization, and the reverse transition — condensation. In all these phase transitions (transformations), a body either liberates or absorbs energy in the form of the latent heat of the relevant transition (the heat of fusion, the heat of vaporization, etc.).

*Phase transitions attended by a stepwise change in the energy or other quantities connected with the energy such as the density are called phase transitions of the first kind* or *first-order transitions.*

First-order transitions are characterized by a stepwise change in the properties of substances, i.e. a change occurring within a very narrow temperature interval. We can therefore speak of a definite transition temperature or point: the melting point, boiling point, etc.

The transition temperatures (points) depend on an external parameter — the pressure $p$. At a given temperature, equilibrium of the phases between which a transition occurs sets in at a quite definite pressure. The line of phase equilibrium is described by the Clapeyron-Clausius equation (7.58) which we have already become acquainted with:

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$

where $L$ = molar heat of transformation
$V_1$ and $V_2$ = molar volumes of the two phases.

In first-order phase transitions, the new phase does not appear immediately throughout the entire volume. First seeds of the new phase form which then grow and spread over the whole volume.

We encountered the process of seed formation when considering the condensation of a vapour into a liquid. For condensation to occur, it is necessary to have centres (seeds) of condensation in the form of dust particles, ions, etc. In exactly the same way for the solidification of a liquid, it is necessary to have centres of crystallization. In the absence of such centres, the vapour or liquid may be in the supercooled state. We can observe pure water at a temperature of −10 °C, for instance, for quite a long time.

Phase transitions are encountered, however, in which the transformation occurs immediately throughout the entire volume as a result of a continuous change of the crystal lattice, i.e. of the mutual arrangement of the particles in the lattice. The result may be that at a definite temperature the symmetry of the lattice changes, for example a lattice having a lower symmetry transforms into one having a higher symmetry. This temperature will be the point of the phase transition, which in this case is called a *phase transition of the second kind,* or a *second-order transition.* The temperature at

which a second-order transition occurs is called the *Curie point* after Pierre Curie who discovered a second-order phase transition in ferromagnetics.

With such a continuous change of state at the transition point, there will be no equilibrium of two *different* phases because the transition occurs immediately throughout the entire volume. Therefore, at the transition point there is no jump of the internal energy $U$. Hence, such a transition is not attended by the liberation or absorption of the latent heat of transition. But since the substance is in different crystalline modifications at temperatures above and below the transition point, these modifications have different heat capacities. This means that the heat capacity, i.e. the derivative of the internal energy with respect to the temperature $dU/dT$, changes stepwise at the point of a phase transition.

The cubic expansion coefficient $(1/V)(dV/dT)$ also changes stepwise, although the volume itself does not change at the point of transition.

Second-order transitions are known upon which a continuous change of state does not signify a change of the crystalline structure, but upon which the state also changes immediately throughout the entire volume. The best-known transitions of this kind are the transition of a substance from the ferromagnetic state to the non-ferromagnetic one which occurs at the temperature called the Curie point, and the transition of certain metals from the normal to the superconducting state in which electrical resistance vanishes. In both cases, no changes in the structure of a crystal occur at the transition point, but the state does change continuously and immediately throughout the whole volume. The transition of liquid helium from the state He I to the state He II is also a second-order transition. In all these cases, a jump in the heat capacity is observed at the transition point. (In this connection, the temperature of a second-order transition has a second name — it is called the *lambda point* according to the nature of the curve showing the change in the heat capacity at this point; this was already mentioned in Sec. 8.9.)

Let us now consider in somewhat greater detail how phase transitions occur. The main part in them is played by fluctuations of physical quantities. We have already encountered them in discussing the cause of the Brownian motion of solid particles suspended in a liquid (Sec. 1.7).

Fluctuations — chance changes of the energy, density, and other quantities related to them — always exist. But far from the point of a phase transition they appear in very small volumes and immediately again resolve. When the temperature and pressure in a substance, however, are close to the critical values, the appearance of a new phase is possible in a volume in which fluctuations are occurring. The entire difference between first-order and second-order phase transitions consists in that the fluctuations near the transition point develop differently.

We have already noted above that in a first-order transition the new phase appears in the form of seeds inside the old phase. The reason for their appearance are chance fluctuations of the energy and density. As the transition point is approached, the fluctuations resulting in the new phase occur

more and more frequently, and although each fluctuation covers a very small volume, all of them together can result in the appearance of a macroscopic seed of the new phase if there is a centre of condensation at the place of their formation.

Matters are much more complicated in a second-order transition. Since the new phase appears immediately throughout the entire volume, the usual microscopic fluctuations cannot by themselves result in a phase transition. Their nature appreciably changes. As the substance approaches the critical temperature, the fluctuations "preparing" the transition to the new phase cover a greater and greater part of the substance and, finally, at the transition point become infinite, i.e. occur throughout the entire volume. Below the transition point, when the new phase has already set in, they again begin to attenuate and gradually become short-lived.

A second-order phase transition *is always connected with a change in the symmetry of a system:* in the new phase either order appears that was absent in the original phase (for example the magnetic moments of separate particles become ordered in a transition to the ferromagnetic state) or already existing order changes (in transitions with a change in the crystalline structure). This new order is also present in the fluctuations near the point of phase transition.

An excellent illustration to the above mechanism of a transition is the well-known "effect of a staring crowd" (Fig. 185). Let us imagine passers-by walking along a sidewalk and looking in the most chance directions. This is the "normal" state of a street crowd in which there is no order. Now let

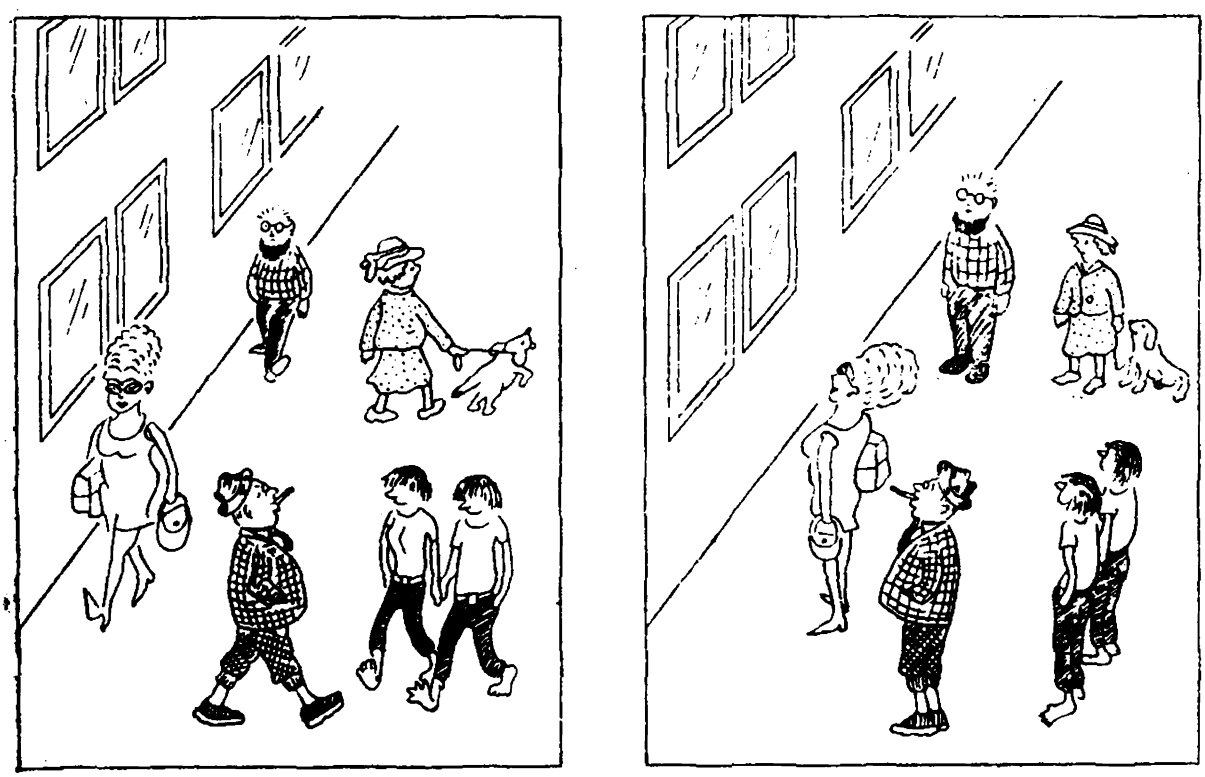


Fig. 185

one of the passers-by without any visible reason begin to stare at an empty window in the second storey of the building (a "chance fluctuation"). Gradually more and more people will begin to look at the same window, and finally everyone nearby will be looking at the same point. An "ordered" phase has appeared, although there are no external forces facilitating the establishment of order — absolutely nothing is occurring behind the window in the second storey!

Second-order phase transitions are a very complicated and interesting phenomenon. The processes occurring in the direct proximity of the transition point have not yet been investigated to the end, and a complete picture of the behaviour of physical quantities in the conditions of infinite fluctuations is only being created.

## 9.14. SOLID HELIUM

Helium, the only substance that does not solidify down to absolute zero, is an interesting exclusion among all substances.

We have already learned that liquid helium is known in two modifications which if helium is under the pressure of its saturated vapour transform into each other at 2.19 K (the lambda point). This is a second-order transition. Particularly, there is no latent heat of transformation in the transition He I-He II.

The phase diagram of helium in connection with the above features of its liquid state has a very peculiar appearance and is unique. It is shown in Fig. 186 (the curves in the figure are not completely to scale): Curve *1* is

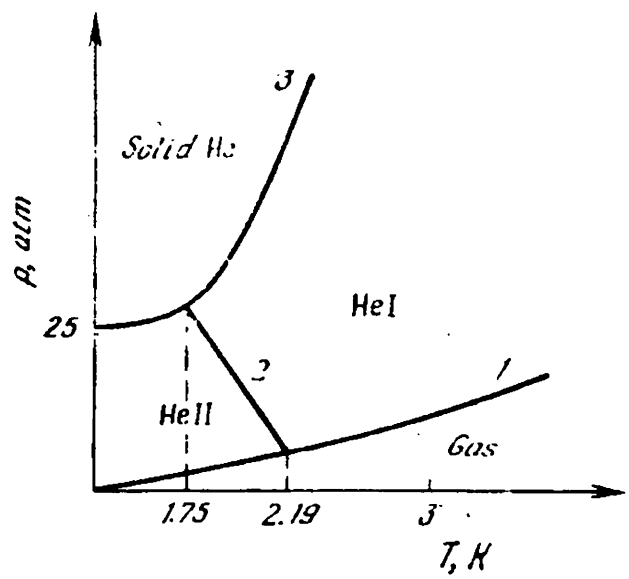



Fig. 186

the vaporization curve. Curve *2* is the line of lambda points. It shows how the He I-He II transition temperature changes with increasing pressure. Finally, curve *3* is the melting-point curve. All these curves divide the dia-

gram into four parts: into the regions of existence of gaseous helium, liquid He I, liquid He II, and solid helium. A glance at the diagram shows that the region of liquid He II extends to absolute zero. This means that at absolute zero too the stable state of helium is the liquid state. As regards solid helium, inspection of the diagram shows that it can be obtained only at an increased pressure which even at absolute zero must be at least 25 atm. And the higher the temperature, the greater is the pressure which is needed for solidification of helium. For example at 50 K, helium freezes at 7000 atm.

The melting-point curve is naturally the curve of equilibrium between solid helium and liquid He I (to the right of the line of lambda points) and between solid helium and liquid helium II (to the left of this line). The vaporization curve is also a line of equilibrium between gaseous helium and the two phases of liquid helium to the left and the right of this line, respectively. But the line of lambda points is not the equilibrium line for the two liquid phases.

A very interesting feature of the phase diagram of helium is the absence of the equilibrium line between the solid and gaseous phases. This means that solid helium cannot be in equilibrium with its vapour in any conditions. Only liquid He I or He II can be over solid helium, but never the gaseous element. Hence, the sublimation of helium is impossible.

All these features of helium, in particular the fact that it also remains liquid at absolute zero, can be explained only on the basis of the quantum theory. Helium is the only substance in nature in which the effects following from the quantum theory are reflected in its macroscopic properties.

The matter is that according to the quantum theory the energy of particles at absolute zero does not equal zero, as follows from the classical kinetic theory of a substance. Even at absolute zero, particles have the so-called zero energy which is the greater, the smaller is the mass of the atoms. Helium atoms therefore have an especially great zero energy (the greatest after hydrogen). On the other hand, owing to the features of the structure of a helium atom, the forces of interaction between helium atoms (as between the atoms of the other inert gases) are very small. It is thus natural that with these small forces of interaction between the atoms, the zero energy is sufficient to prevent the helium atoms from being arranged in regular order, i.e. from forming a crystal lattice. And only an external pressure can bring the atoms close enough together for them to form a crystal.

The distinctive feature of helium is exactly the fact that at low temperatures its behaviour is determined by the zero energy and not by the energy of thermal movements.

The zero energy ought to play a still greater part in hydrogen whose atoms have a still smaller mass. Indeed, hydrogen atoms do have a greater zero energy than helium atoms. But we have just seen that the decisive part is played by the ratio between the zero energy and the energy of interaction

of the particles. The latter is much greater for hydrogen atoms than for those of helium. A numerical assessment shows that in solid hydrogen the zero energy is half of the total energy whereas in helium it is about 80% of the total. This is precisely the explanation of the low temperature of liquefaction of helium and the impossibility of its solidification in ordinary conditions. The zero energy plays a still greater part in the light helium isotope $He^3$. Here the zero energy is 95% of the total. Therefore the liquefaction point (at normal pressure) is still lower for $He^3$ (3.2 K instead of 4.2 K for ordinary helium). An even greater pressure than for $He^4$ is needed to solidify $He^3$—over 29 atm at absolute zero.

## 9.15. DISSOLUTION AND CRYSTALLIZATION FROM A SOLUTION

Apart from melting and vaporization, a crystal lattice can be destroyed by the dissolution of a solid in a suitable solvent.

Owing to the interaction of the particles of a crystal and the solvent, the forces retaining the atoms in the lattice points may diminish to such an extent that the thermal movements will be sufficient for destruction of the lattice. As a result, the dissolved substance, called a solute, forms together with the solvent a homogeneous mixture — a solution. The basic characteristic of a solution is its concentration, i.e. the content of the mass of the solute (in per cent) in the mass of the solution. In addition to the pressure and the temperature, the concentration is an important parameter of state of a solution (see Sec. 7.14).

The dissolution of a solid in a liquid is usually attended by cooling of the solution. This occurs because dissolution is the destruction of a crystal lattice, and a certain energy is always needed for such destruction. When a lattice is destroyed in melting, the energy is supplied by the source of heat. In dissolution, however, the lattice is destroyed at the expense of the internal energy of the solvent, and this results in cooling of the solution.

Dissolution may also occur in isothermal conditions, but in this case heat must be supplied from outside. The quantity of heat needed for the isothermal solution of a unit mass of a substance is called the *specific heat of solution.* The stronger the bonds between the particles of a crystal, the greater is the heat of solution.

Cooling in dissolution is one of the ways of obtaining low temperatures. It is general knowledge that snow and ice cool when mixed with sodium chloride or calcium chloride. In the first case, a temperature of about −20 °C can be obtained, and in the second as low as −55 °C. The freezing point of a solution is always lower than that of the pure solvent because the forces of the bonds between the particles diminish in dissolution.

It is usually possible to dissolve not more than a quite definite amount (maximum) of the solute in a given amount of the solvent. A solution

having such a maximum concentration is called a *saturated solution*. The value of the maximum concentration is called the *solubility* of a substance in a given solvent. The solubility grows with increasing temperature so that a solution which is saturated at a certain temperature becomes unsaturated at a higher one, and supersaturated at a lower one.* In the latter case when centres of crystallization are present, the surplus part of the solute crystallizes from the solution, precipitating in the form of small crystals until the solution becomes saturated. Crystallization from a solution can also be conducted without supersaturation of the solution by lowering the temperature. Crystals will also precipitate upon evaporation of the solvent.

Crystallization from a solution is one of the important ways of obtaining artificial monocrystals. It is easy to obtain monocrystals in this way (sometimes of a considerable size) with regular faceting.

**Lowering of the Freezing Point in Solutions.** We saw in Sec. 7.14 that the change in the forces of interaction between the particles in a solution results in a change in the saturated vapour pressure and the boiling point of the solution in comparison with the pure solvent. It is clear that if the bonding forces in a solution lower, this should result in lowering of the freezing point of the solution in comparison with the pure solvent. Such lowering does occur, and it depends on the concentration of the solute and on the heat of fusion of the solvent.

Using Raoult's law and the Clapeyron-Clausius equation, we can get an expression for the magnitude of the change in the freezing point $\Delta T_{fr}$ which is absolutely the same as the one we obtained for elevation of the boiling point:

$$\Delta T_{fr} = \frac{RT_{fr}^2}{L} x_2$$

or

$$\Delta T_{fr} = \frac{RT_{fr}^2}{L} \frac{m\mu}{1000} \tag{9.22}$$

where $\Delta T_{fr}$ = difference between the freezing points of the pure solvent and the solution — the depression or lowering of the freezing point

$T_{fr}$ = freezing point of the pure solvent

$x_2$ = mole fraction of the solute in the solution

$\mu$ = molecular weight of the solute

$m$ = molality of the solution

$L$ = heat of fusion of the pure solvent.

* An exception is sodium chloride (NaCl) whose solubility in water does not virtually depend on the temperature.

Equation (9.22) is used to determine the molecular weight of a solute according to the lowering of the freezing point of a solution. This method of measuring $\mu$ is called the *cryoscopic method.*

We shall see in the following section that a solution when cooled does not solidify completely at a definite temperature (an exception is a solution of a definite, so-called *eutectic* concentration). Therefore, by $\Delta T_{fr}$ should be understood the temperature of the beginning of freezing when solid crystals of the solvent appear in the liquid solution (see below).

## 9.16. ALLOYS. FUSIBILITY DIAGRAMS

An alloy is a mixture of two or more substances, for example metals. Hence, an alloy is also a solution of one substance in another.

It is convenient to depict the processes of melting and solidification of alloys in phase diagrams (they are sometimes also called fusibility diagrams). If we previously described the state of one-component substances by means of two parameters, for instance the pressure and temperature (the third parameter is unambiguously determined by the two named ones), then for a two-component or binary alloy (which are the only ones that will be considered here), we must also know a third parameter, for example the concentration. Consequently, the states corresponding to the equilibrium of any two phases are graphically depicted by a surface instead of by a straight line. We shall use a two-dimensional temperature-concentration diagram, however, assuming the pressure to be constant. This diagram is therefore a section of a three-dimensional surface with a plane $p = \text{const}$.

Thus, let us cool a binary alloy. At a certain temperature it begins to solidify, and this may occur differently. We shall consider only two very simple cases here. First, the crystals formed may each contain only one of the components so that the solidified alloy consists of tiny crystals of both constituent parts of the alloy instead of containing a mixture of atoms in a single lattice.

Second, the crystals forming upon solidification may consist of atoms of both components occupying the points of a common crystal lattice with equal rights. In the latter case, a *solid solution* is said to form.

Let us first consider a phase diagram for systems of the first kind. A very simple diagram for this case is shown in Fig. 187. The diagram shows how the melting point depends on the composition of an alloy consisting of two components A and B. We lay off the concentrations of the two components from the left and from the right along the axis of abscissas, the concentration of component A growing from the right to the left so that point $A$ corresponds to the pure substance A (concentration 100%). The concentration of component B grows from the left to the right so that point $B$ corresponds to the pure substance B.

The melting points of the alloys are laid off along the axis of ordinates. Points $t_A$ and $t_B$ are the melting points of the pure components A and B.

From what has been said above about the freezing point of solutions, it follows that it must lower with a growth in the concentration of A and that of B. Such a course of the solidification (freezing) point is observed experimentally, as is shown in Fig. 187. Beginning from point $t_A$, the melt-

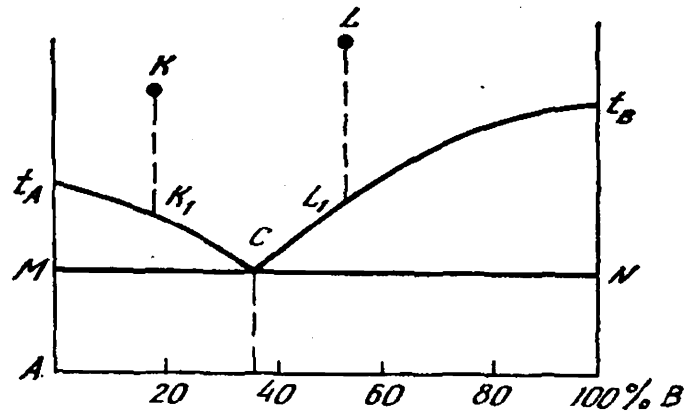



Fig. 187

ing point of component A lowers with an increasing concentration of component B. In exactly the same way, the solidification point of substance B lowers with an increasing concentration of component A.

Therefore, both melting-point curves converge at a certain point. This point C gives the lowest melting (solidification) point that an alloy of the given system can have, and also the concentration of the components of this alloy having the lowest melting point. An alloy having such a composition is called a *eutectic*. Point C is called the *eutectic point*.

If we cool an alloy whose concentration corresponds to point $K$ to the left of the eutectic composition, then when the temperature reaches point $K_1$, component A begins to freeze out and precipitate from the solution in the form of crystals in a liquid alloy. The concentration of component B in the remaining alloy grows, and this causes a further depression of the freezing point. Thus, lowering of the temperature is attended by a constant change in the composition of the liquid alloy until at point C it solidifies completely forming a homogeneous mechanical mixture of the crystals of both components characteristic of a eutectic.

In exactly the same way upon cooling of an alloy whose concentration corresponds to point $L$ (to the right of the eutectic point), crystals of component B will begin to precipitate after the temperature has lowered to point $L_1$. This will cause further lowering of the melting point owing to the growth in the concentration of component A. The alloy will solidify completely at the temperature and concentration corresponding to eutectic point C.

If we cool a liquid alloy of the eutectic concentration, at a temperature corresponding to point C it will completely solidify immediately.

There is no need to mention here that when a solid alloy is heated the process occurs in the reverse sequence to that described above.

The region of temperatures and concentrations above line $t_A C t_B$ is the region of the liquid phase. The region between this curve and the horizontal line passing through the eutectic point (line $MN$ in Fig. 187) is a region in which crystals of components A or B are in the liquid alloy. Finally, the region below line $MN$ is the region of the solid state; in its left-hand part crystals of A are interspersed among the eutectic, and in its right-hand part crystals of B are interspersed among the eutectic.

Thus a feature of alloys is that they solidify not at a definite temperature like one-component substances, but within a certain temperature interval. Solidification begins on line $t_A C t_B$ (it is often called the *liquidus line*) and terminates on line $MN$ — the horizontal line passing through eutectic point $C$ (this line is called the *solidus line*). Only an alloy having the eutectic composition solidifies immediately at the temperature corresponding to point $C$.

An example of a binary system with a phase diagram of the kind shown in Fig. 187 is the system tin-zinc. Tin melts at 232 °C, zinc at 419 °C, and the melting point of the eutectic (8% of zinc) is 199 °C.

For alloys of the second kind, i.e. for alloys forming solid solutions, the phase diagram has a somewhat different appearance. A typical diagram of this kind is shown in Fig. 188. Here again, we have laid off the concentrations of the components and the melting point along the axes of coordinates. The region above the "cigar-shaped" curve $t_A C t_B C'$ is the region of the liquid state of the alloy, and the region below it that of the solid state. Curve $t_A C t_B$ is the dependence of the solidification point of the liquid alloy on its composition (the liquidus line). Lower curve $t_A C' t_B$ gives the dependence of the melting point of the solid alloy on the concentration. Hence, at the same composition of the alloy, its melting point differs from its solidification point; the solid alloy melts at one temperature, and the liquid one freezes at another. Conversely, at the same temperature, a liquid of one composition crystallizes, and a solid alloy of a different composition melts.

Here again, solidification and melting occur not at a single definite temperature, but within a certain temperature interval. Thus, if we cool a liquid alloy having the composition shown by point $K$, then when a temperature corresponding to point $K'$ is reached, crystals begin to freeze out whose composition, however, is determined by point $K''$ instead of point $K$. They will therefore contain more of component B than the liquid alloy. Consequently, the liquid will become richer in component A, and the freezing point will lower along curve $t_A C' t_B$.

The region confined within the "cigar-shaped" curve thus corresponds to a mixture of the liquid alloy and crystals of the solid solution.

Sometimes, phase diagrams of alloys have the form shown in Fig. 189. The "cigar" here is "crushed" so that the solidus and liquidus curves have a minimum, and at the point of the minimum the two curves merge. An alloy having the composition corresponding to the point of merging solid-

ifies and melts immediately at a definite temperature as occurs with the eutectic in alloys of the first kind.

Phase (fusibility) diagrams are constructed experimentally on the basis of the so-called thermal analysis. The latter consists in obtaining curves

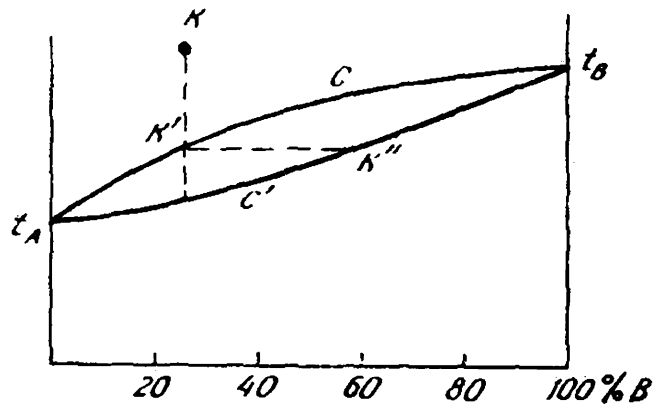



Fig. 188

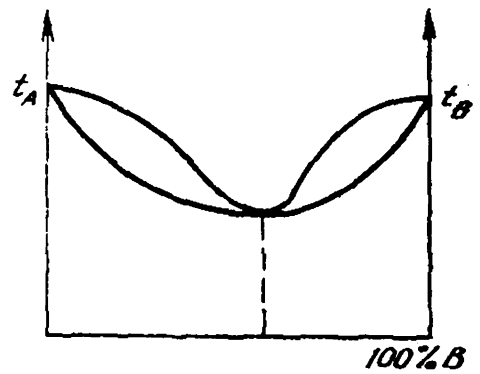



Fig. 189

of the cooling and heating of mixtures of different compositions of the components being studied. These measurements give data on the temperatures of the beginning and end of crystallization that are used to construct the graphs described above (see below).

In addition, so-called property-composition diagrams are constructed for a detailed analysis of the features of systems and of the interaction of their components with one another. These diagrams are curves showing how a quantity characterizing a property of the system (hardness, electrical resistance, viscosity, etc.) depends on its composition at a constant temperature. Such diagrams together with phase diagrams serve as the basis for the so-called physicochemical analysis of binary and more complicated systems developed by N. Kurnakov.

## 9.17. ZONE PURIFICATION OF METALS

The phase diagram of a binary system forming solid solutions depicted in Fig. 188 shows that the solid and liquid states of the substance of an alloy can be in equilibrium having different concentrations of the components. Thus, upon the cooling of an alloy from point $K$ corresponding to a liquid solution to point $K'$ on the liquidus line (see Fig. 188), solid crystals will appear in the liquid alloy having a content of the components corresponding to point $K''$ instead of $K'$. For the case shown in Fig. 188, the content of component B in a solid crystal is thus greater than in the liquid with which it is in equilibrium.

This occurs when an addition of component B raises the melting point of substance A. If substance B lowered the melting point of substance A instead of raising it, the phase diagram for such a system would have the

form shown in Fig. 190. Now the concentration of component B in the crystals freezing out upon cooling would be smaller than in the liquid with which they are in equilibrium.

The circumstance that the concentration of one of the components of an alloy in the solid and liquid phases neighbouring with each other may be different is used for purifying (refining) metals from admixtures in the so-called *zone-melting process.*

Here we are speaking about the removal from a metal (or some other substance) of the usually small foreign impurities that remain in them in the process of their preparation and that are exceedingly difficult to remove in any other way. This is a very important task that is encountered not only in scientific research, but also in quite significant branches of engineering.

The zone-melting refining process consists in creating a narrow molten zone in the specimen to be purified with the aid of a heater, this zone mov-

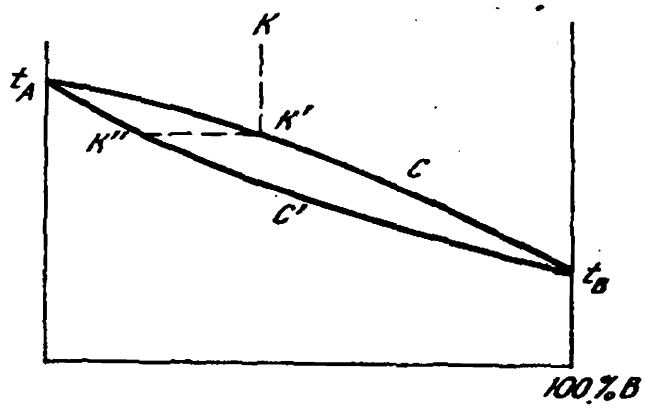



Fig. 190

ing along the specimen (Fig. 191). Movement of the zone is achieved either by the heater travelling along the specimen or by the specimen travelling past a stationary heater.

Upon travelling along the specimen, the molten zone leaves behind itself a region of a solidified melt neighbouring with the liquid phase of the zone. If the impurity lowers the melting point of the basic substance (see Fig. 190), then the concentration of the impurity in the molten zone will be greater than in the solidified phase behind it. Hence, the impurities have partly left the solid phase, passed over into the liquid phase and move together with it along the specimen. The maximum concentration of the impurities will be found in the extreme right-hand part of the specimen which the molten zone arrives at in the long run (see Fig. 191). The left-hand part will be depleted of the impurities, i.e. partly purified.

During one pass of the zone, the degree of purification achieved is comparatively small, and the purified region is mainly the edge of the specimen. But the effectiveness of the process can be considerably increased if the passage of the molten zone along the specimen is repeated many times.

This can be done, for instance, by using not one, but several heaters following one another as shown in Fig. 192.

The result of purification in zone melting depends on very many factors and primarily on the properties of the substance being purified and the impurities in it. One of the most important factors which the effectiveness

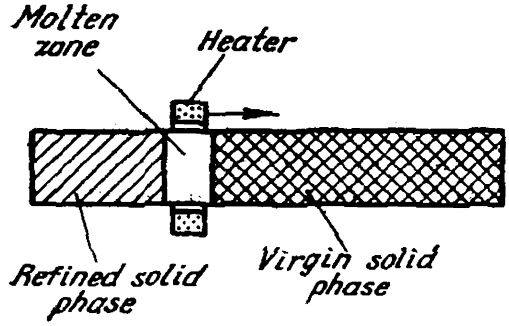



Fig. 191

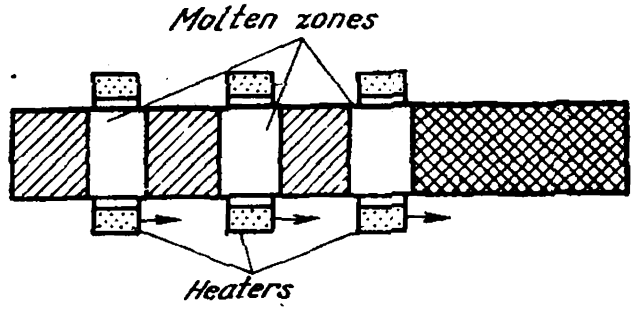



Fig. 192

of zone purification depends on is the so-called *distribution* or *partition coefficient* $K$ equal to the ratio between the concentrations of the impurity in the solid ($c_s$) and liquid ($c_{lq}$) phases:

$$K = \frac{c_s}{c_{lq}} \tag{9.23}$$

In systems in which the impurity lowers the melting point of the basic substance, the coefficient $K$ is less than unity. In systems where the impurity raises the melting point, $K$ is greater than unity. When $K$ equals unity, purification by the zone-melting process is naturally impossible because the process is based on the difference between the concentrations $c_s$ and $c_{lq}$. It is obvious that zone melting is the more effective, the smaller is the partition coefficient (for systems with phase diagrams of the kind shown in Fig. 190).

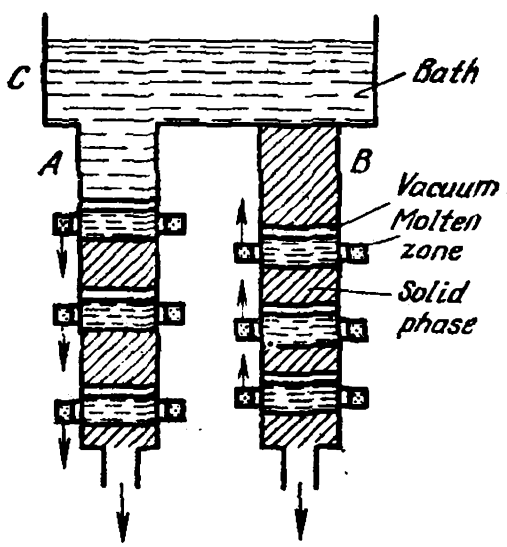



Fig. 193

In the zone-melting process described above, the purification of a specimen is periodical. But it can be made continuous if the zone-melting installation is provided with a source of supply of the material being purified and the purified and contaminated products are removed in the course of operation. Such an installation is shown in Fig. 193. It consists of two vertical tubes $A$ and $B$ and bath $C$ with the molten material that feeds the installation. The heaters in the left-hand tube create molten zones and move them downward. Therefore, the contaminated product gathers in the lower part of this tube and is discharged outward. The heaters in the right-hand

tube, on the contrary, move upward together with the molten zones. The purified product gathers in the lower part of this tube, and an outlet is also provided for it. The vacuums appearing when the contaminated and the purified products are discharged rise to the surface, thus ensuring motion of the material in the installation. This is why the above process of continuous refining is often called the *zone-vacuum process.*

The zone-melting process makes it possible to obtain very high degrees of purification. For example, this process yields germanium (it is exactly for purifying this metal that the zone-melting process was first developed) having a concentration of impurities of about $10^{-7}$ %. Other metals and semiconductors having an unprecedentedly small content of impurities are also produced by this process. It can be used for purifying not only metals and semiconductors, but also various organic and inorganic compounds, etc.

Zone melting is used not only for the simple purification of materials from admixtures. It helps to solve some other problems including ones that cannot in general be solved in other ways. For instance, a variant of zone melting has been developed that ensures strictly uniform distribution of the impurities in a specimen *(zone levelling)*, which is very important in the production of semiconductor appliances. Zone melting also makes it possible, apart from the purification of a substance, to grow monocrystals from it, introduce and distribute admixtures in them, etc. In general, it is a process of controlling admixtures or impurities in a substance. It is not surprising that it is finding new and new applications, and that the number of substances which it can be used for is constantly growing.

## 9.18. EXPERIMENTAL DETERMINATION OF MELTING POINT

There are many different ways of determining the melting point. One of the most frequently used methods is to obtain a melting-point or freezing-point curve, i.e. a curve showing how the temperature of a substance being melted or solidifying depends on the time with the external conditions naturally being constant. We have already noted that such curves (see Fig. 179) have a horizontal portion indicating the discontinuation of the change in temperature (heating or cooling) of the relevant substance. The temperature corresponding to this portion is the melting point of the substance, which coincides (for pure substances) with the freezing or solidification point.

To plot such a curve, a vessel (crucible) with the substance being studied is placed in a furnace where it is heated and the temperature is measured at definite intervals of time (the thermometer must be in direct contact with the substance). Customarily not a melting-point curve, but a freezing-point curve is obtained with the measurements beginning at a temperature that is from 10 to 20 kelvins higher than the melting point. After plotting a

graph of the temperature $T$ against the time $t$, it is a simple matter to determine the melting point $T_m$ (or the freezing point $T_{fr}$).

To facilitate measurements, a small rate of cooling should be used — about two kelvins a minute. It is good practice to agitate the crucible during the experiment to avoid temperature gradients appearing in the bulk of the molten substance.

It is naturally important to see that the materials of the crucible, the thermometer, and of other parts in contact with the substance being studied do not contaminate it because impurities may change the melting point.

The above simple method of determining the melting point can also be used for measuring the latent heat of fusion. For this purpose, however, a curve of heating during melting must be obtained.

The heat of fusion is determined from the width of the horizontal section on this curve which obviously gives the value of the time interval $\Delta t$ during which the heat of fusion is absorbed. If an electric furnace is used for the experiment, then each second it liberates a quantity of heat equal to $0.239UI$, where $U$ is the potential difference across the ends of the furnace winding, and $I$ is the current in it. During the time $\Delta t$ (the width of the horizontal portion of the curve), therefore, $0.239UI\,\Delta t$ calories will be liberated. If the mass of the substance in the crucible is $m$, then the latent specific heat of fusion $L$ is determined by the expression

$$L = \frac{0.239UI\,\Delta t}{m} \text{ cal/g} \quad \text{or} \quad L = \frac{1.001UI\,\Delta t}{m} \text{ J/g} \qquad (9.24)$$

It goes without saying that when determining $L$, instruments for measuring $U$ and $I$ must be included in the electric circuit of the furnace. It is also necessary to ensure reliable thermal insulation of the furnace. This will allow us to consider that the heat $0.239UI\,\Delta t$ has indeed been spent for melting the substance.

The melting point is also often determined by observing the sharp stepwise changes in some of the physical properties of a substance when it passes through the melting point. These properties include, for example, the electrical resistance, specific volume, and the magnetic properties.

## 9.19. THERMAL PROPERTIES OF SOLIDS

**Thermal Motion in Solids.** We have already mentioned that the thermal movements of the particles in a solid are not the same as in a fluid. The particles of a solid connected to one another by the forces of interaction depending on the interatomic distances can only oscillate about a certain equilibrium position at the points of a crystal lattice. Since a substance can be solid only at sufficiently low temperatures when the energy of the thermal movements, i.e. $kT$, is much smaller than the potential energy of interaction of the particles with one another, the oscillations of the atoms about their

equilibrium positions are small ones. The energy of these oscillations is the internal energy of the solid that determines its temperature.

At absolute zero, all atomic movements cease. A crystal must be completely ordered for its entropy to equal zero. But the quantum theory arrives at the conclusion that at absolute zero too, particles have a certain energy which is the greater, the smaller is the mass of the particle. This energy cannot be taken away from the particles in any conditions. The presence of such a *zero* energy does not prevent the entropy of a solid at absolute zero from equalling zero because the entropy is connected with chaotic thermal motion while the zero energy is not thermal. And if a crystal has no defects, its entropy tends to zero as absolute zero is approached.

The zero energy is usually considerably smaller than the energy of interaction between particles so that it does not hinder the solidification of a substance. And only in a single case, namely, in the case of helium, does the zero energy play such an important part that the solidification of helium becomes impossible without the action of an external pressure. All other substances solidify before their zero energy can noticeably affect their properties.

**Heat Capacity of Solids.** Thus, a solid is a complex of oscillating particles, vibrators. When heat is supplied to a body, it is used to increase the energy of the oscillations of the vibrators, which consists of the kinetic and potential energies. If the oscillations are harmonic, both these parts of the total energy equal each other.

Each oscillation can be resolved into three components along the axes of coordinates, and the energy of each component is also expressed by the sum of the potential and kinetic energies equal to each other.

We know from the kinetic theory of gases that the mean kinetic energy of an atom along one of the axes is $kT/2$. This is the kinetic energy per degree of freedom. But since the potential energy of a vibrator equals its kinetic energy, then the total energy per degree of freedom equals $2\times kT/2 = kT$.

We know that each atom (vibrator) has three degrees of freedom, and if we assume, as we did in the theory of ideal gases, that the same kinetic energy $kT/2$ falls to each degree of freedom, then the total energy of one atom of a solid is $3\times 2\times kT/2 = 3kT$.

If a body contains $N$ atoms, then the internal energy of the body is $3NkT$. Thus, the internal energy of one mole equals $3N_Ak T = 3RT$, where $N_A$ is the Avogadro constant.

When heat is supplied in conditions of a constant volume, all the heat goes to increase the internal energy. Hence, the atomic heat capacity at constant volume is determined by the equation

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3R \approx 6 \text{ cal/mol}\cdot\text{K} \approx 25.12 \text{ J/mol}\cdot\text{K} \qquad (9.25)$$

This is double the molar heat capacity of an ideal gas (monoatomic). Consequently, it is sufficient to transfer a substance from the gaseous to

the solid state for its molar heat capacity to double. It is obvious from the above that the heat capacity doubles because upon heating a solid the supplied heat is spent for increasing not only the kinetic, but also the potential energy of the particles.

It follows from Eq. (9.25) that the atomic heat capacity (i.e. the heat capacity of a gramme-atom) of a solid is a constant quantity identical for all substances and not depending on the temperature. This statement is called the *Dulong and Petit law.*

Experiments show that at ordinary temperatures the atomic heat capacty of most solids (chemical elements) is indeed close to the value of 6 cal/mol·K and does not virtually depend on the temperature. There are exceptions to the rule, however. The heat capacity of four chemical elements — beryllium, boron, silicon, and diamond — at ordinary temperatures is considerably smaller than $3R$ and appreciably depends on the temperature. With elevation of the latter, the heat capacity of these substances grows, tending nevertheless to the value of $3R$.

This is not the only deviation from the Dulong and Petit law. At low (much lower than room) temperatures, the heat capacity of all substances, including those that obey the Dulong and Petit law at ordinary temperatures, rapidly diminishes and tends to zero at the absolute zero of the temperature scale. Figure 194 gives an experimentally obtained curve showing

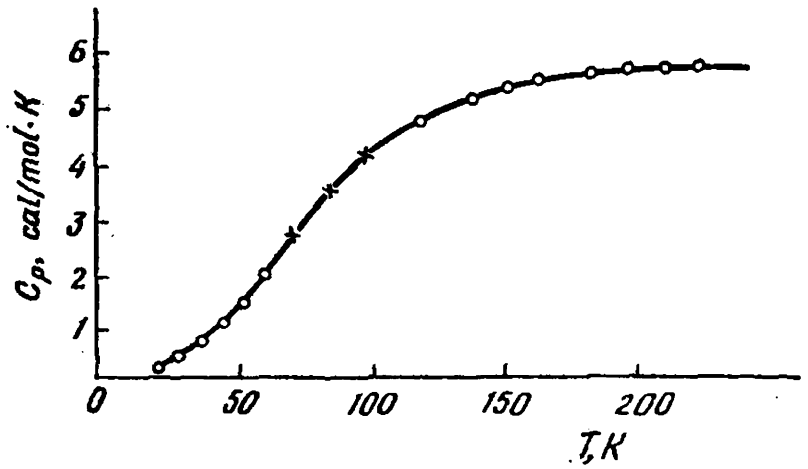



Fig. 194

how the heat capacity $C_p$ (it is the heat capacity at constant pressure that is determined experimentally) depends on the temperature for silver.

Numerous experiments have shown that it is not the Dulong and Petit law which is common for all solids, but deviations from it. Indeed, the heat capacity of solids depends on the temperature, and in such a way that it diminishes in proportion to the cube of the temperature when the latter lowers and tends to zero at absolute zero. Therefore, the elements beryllium, boron, silicon, and diamond are the rule rather than an exception from it, but room temperature is a low one for them.

We have seen that the Dulong and Petit law is a corollary of the law of uniform distribution of energy among the degrees of freedom. Hence, the circumstance that solids do not actually obey the Dulong and Petit law at low temperatures shows that the hypothesis on the uniform distribution of the energy by degrees of freedom is approximate.

The experimentally observed temperature dependence of the heat capacity can be explained on the basis of quantum notions.

It was indicated above that the molecules of a solid are vibrators. According to the quantum theory, the energy of a vibrator is an integral factor of the quantity $h\nu$, where $\nu$ is the frequency of oscillations of the vibrator, and $h$ is the Planck constant equal to $6.6 \times 10^{-34}$ J·s ($6.6 \times 10^{-27}$ erg·s). Thus, the energy of an oscillating molecule can be written in the form

$$E = nh\nu \tag{9.26}$$

where $n$ is any integer. For different molecules of a solid, the quantity $\nu$ may be different, and their energy will differ accordingly. We shall assume for simplicity, as A. Einstein did, that all molecules oscillate with the same frequency, which is actually not correct.

What is the mean energy $\bar{E}$ of one molecule?

Using the Boltzmann equation (1.42), we can find what part of the molecules have the energy $E = nh\nu$:

$$N = N_A \exp\left(-\frac{nh\nu}{kT}\right) \tag{9.27}$$

Therefore, the mean energy of a molecule $\bar{E}$, equal to the ratio of the sum of the energies to the sum of the number of molecules, is determined by the expression

$$\bar{E} = \frac{\sum\limits_n EN_A \exp\left(-\frac{nh\nu}{kT}\right)}{\sum\limits_n N_A \exp\left(-\frac{nh\nu}{kT}\right)} = \frac{h\nu \sum\limits_n n \exp\left(-\frac{nh\nu}{kT}\right)}{\sum\limits_n \exp\left(-\frac{nh\nu}{kT}\right)}$$

or, letting $x$ stand for $h\nu/kT$, we get

$$\bar{E} = \frac{h\nu \sum\limits_n ne^{-nx}}{\sum\limits_n e^{-nx}} \tag{9.28}$$

For great values of $n$, we have

$$\frac{\sum\limits_n ne^{-nx}}{\sum\limits_n e^{-nx}} = -\frac{d}{dx} \ln \sum_n e^{-nx} = -\frac{d}{dx} \ln \frac{1}{1-e^{-x}} = \frac{1}{e^x - 1}$$

and Eq. (9.28), remembering that $x = h\nu/kT$, becomes

$$\bar{E} = \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \tag{9.29}$$

Thus, unlike the classical theory according to which the mean energy of one molecule $\bar{E} = kT$, according to the quantum theory it is determined by Eq. (9.29).

It is easy to see that for high temperatures, when $kT \gg h\nu$, both expressions coincide. Indeed, if we limit ourselves to the first two terms of the expansion of the function $\exp(h\nu/kT)$ into a series, we get

$$\exp\left(\frac{h\nu}{kT}\right) = 1 + \frac{h\nu}{kT}$$

and Eq. (9.29) becomes

$$\bar{E} = \frac{h\nu}{1 + \frac{h\nu}{kT} - 1} = kT$$

The energy of one mole, instead of the value $3N_A kT$ according to the classical theory, becomes

$$U = 3N_A \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \tag{9.30}$$

and the heat capacity

$$C_V = \frac{dU}{dT} = 3N_A k \frac{\left(\frac{h\nu}{kT}\right)^2 \exp\left(\frac{h\nu}{kT}\right)}{\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^2} \tag{9.31}$$

At great values of $T$, Eq. (9.31) gives a value for the heat capacity $C_V$ equal to $3R$, i.e. the Dulong and Petit law, while for $T = 0$ the heat capacity becomes equal to zero in complete accordance with experimental data.

The temperature dependence of the heat capacity calculated from Einstein's theory is in general close to that observed experimentally, and only at low temperatures are the discrepancies between theory and experimental data quite appreciable. These discrepancies are naturally explained by the arbitrary nature of the assumption that all the oscillations of molecules of a solid are performed with the *identical* frequency $\nu$. These frequencies are selected so that the values of the heat capacity $C_V$ calculated by Eq. (9.31) will be as close as possible to the experimental data. It is

not surprising that attempts to do this are not successful for all temperatures.

P. Debye, while retaining A. Einstein's basic idea, noticeably improved the theory, assuming that a solid contains a whole set of oscillation frequencies. The set of oscillation frequencies of a system is called a *spectrum*. The oscillations we are treating here are the elastic oscillations that are responsible for the propagation of sound in a solid, and to a first approximation the velocity of sound equals $(E/\rho)^{1/2}$ (here $E$ is the Young's modulus, and $\rho$ is the density of a body).

We encounter a spectrum of frequencies, for example, when considering the oscillations of a string, which are the result of superpositions of the oscillations of an infinite number of overtones onto the fundamental tone of the string.

In the quantum theory, the energy of sound oscillations $h\nu$ is considered as special particles called *phonons* (see Sec. 9.22). The number of possible oscillation frequencies is infinitely great. The number of atoms in a solid body, although very great (of the order of magnitude of $10^{22}$ atoms per square centimetre), is finite, however. It must therefore be assumed, as was done by Debye, that the spectrum of oscillations in a solid is limited by a certain maximum frequency $\nu_{max}$. It follows from Debye's theory that beginning from a certain temperature $\Theta$ (the *Debye characteristic temperature*), the heat capacity begins to rapidly diminish with lowering of the temperature. This is the temperature at which the energy of the thermal movements $k\Theta$ becomes equal to the maximum energy of the vibrators:

$$k\Theta = h\nu_{max}$$

whence

$$\Theta = \frac{h\nu_{max}}{k} \tag{9.32}$$

At temperatures much lower than $\Theta$, the heat capacity diminishes in proportion to the cube of the temperature (the "$T^3$ law") which, as we have seen, corresponds to experimental data.

The Debye temperature $\Theta$ may be considered (and not only with respect to the heat capacity) as the boundary between high and low temperatures.

From the viewpoint of the quantum theory of heat capacity, the fact that some substances (diamond, boron, etc.) do not obey the Dulong and Petit law even at room temperatures is explained by the Debye characteristic temperature being so high for these substances that room temperature must be considered as a low temperature. For example, if the characteristic temperature is 210 °C for silver, about 400 °C for aluminium, and about 90 °C for lead, then for diamond it equals 2000 °C.

Measurements of heat capacity and its temperature dependence play a great part in investigations of solids. This is associated with the fact that

the heat capacity is directly determined by the oscillations of the atoms in a crystal lattice. It is quite obvious that the nature of these oscillations must depend on the structure of the lattice, its symmetry, etc. As a result, the transformations that may occur in a substance are often attended by various anomalies of the heat capacity.

Particularly, second-order phase transitions in which no latent heat is liberated (or absorbed) are attended by a jump in the heat capacity, by a break in its monotonous change with the temperature. We can detect such transitions by investigating the temperature dependence of the heat capacity.

We shall note in conclusion that only the heat capacity at constant pressure lends itself to direct measurement, and not the heat capacity at constant volume because thermal expansion prevents us from ensuring a constant volume of a body. But owing to the small value of the change in volume upon heating, the difference between the heat capacities $C_V$ and $C_p$ is small.

## 9.20. MEASUREMENT OF HEAT CAPACITY

The heat capacity, as we know, is determined by the ratio of the quantity of heat $\Delta Q$ supplied to a body to the increase in the temperature caused by this heat [see Eq. (2.6)]:

$$C = \frac{\Delta Q}{\Delta T}$$

Consequently, to determine the heat capacity $C$, we must supply an accurately measured quantity of heat $\Delta Q$ to the specimen being studied and measure the resulting change in the temperature $\Delta T$.

No serious difficulties are encountered in measuring $\Delta T$. Modern methods of measuring temperatures make it possible to easily measure a small temperature difference with an accuracy up to 0.001 K, and this is usually quite adequate. We can also measure the quantity of heat supplied with a great accuracy. But we must be sure that the supplied accurately measured quantity of heat has indeed been absorbed by the specimen so that the measured change in the temperature $\Delta T$ has been exactly caused by the measured quantity of heat $\Delta Q$. But the heat supplied to a specimen may not be absorbed by it completely. In addition, the specimen may receive heat from other sources or lose it. Hence, there is always a certain indeterminacy in the value of the quantity $\Delta Q$ and, consequently, an error in determining $C$. The efforts of experimenters are directed to a considerable extent at a reduction of these errors in measurements.

The instruments used for measuring the heat capacity are called *calorimeters* (when the heat capacity is known, they are used to measure the quantity of heat).

A very great number of various calorimeters are in use that differ in their design and even in their principle of operation. We shall consider as an

example here the design of one kind of calorimeter that is used quite often in measuring the heat capacity (mainly at low temperatures).

The instrument consists (Fig. 195) of a calorimeter proper—specimen $S$ of the substance being studied with electric heater $R$ wound onto it, and envelope $E$ surrounding the specimen. Heater $R$ simultaneously serves as a resistance thermometer in contact with the specimen. The function of the envelope is to thermally isolate the specimen being studied from the surroundings. Isolation is achieved by evacuating the space inside the envelope up to a high vacuum. The specimen is suspended on thin metal wires also serving to supply current to the heater. In an ideal calorimeter, the envelope must reliably protect the specimen from thermal interaction with the medium surrounding the calorimeter so that the specimen will not receive heat from it nor give up heat to it. The means for supplying heat and measuring the temperature must not violate this isolation.

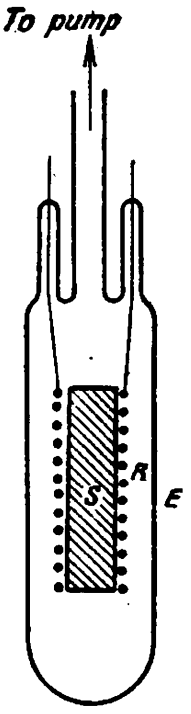


Fig. 195

The measurements in such an ideal calorimeter would consist in the following simple operations. First, without creating a vacuum inside the calorimeter, it is placed in a thermostat (for example in an electric furnace, in a vessel containing a liquid at a given temperature, etc.) so that the specimen will be brought up to the temperature at which the measurements should be conducted. After this, the space inside the calorimeter is evacuated, and the specimen is thus isolated from the thermostat. Next, an electric current is passed through the heater during a definite (accurately measured) time. The potential difference across the heater is measured and the current flowing through it. Having now measured the increase in the temperature caused by the action of the heater, we can calculate the heat capacity of the specimen. By dividing the value of $C$ obtained by the mass of the specimen in grammes or in moles, we get the specific or molar heat capacity, respectively, of the substance which the specimen is made of.

## 9.21. THERMAL EXPANSION OF SOLIDS

It is general knowledge that solids increase their volume when heated. This is *thermal expansion*. Let us consider the reasons why the volume of a body grows when it is heated.

The volume of a crystal evidently grows with an increase in the mean distance between its atoms. Hence, an increase in the temperature leads to a growth in the mean distance between the atoms of a crystal. Why does the distance between the atoms in a crystal grow when the latter is heated?

An increase in the temperature of a crystal denotes a growth in the energy of thermal motion, i.e. in the thermal oscillations of the atoms in the lattice (see Sec. 9.19) and, consequently, a growth in the amplitude of these oscillations.

But an increase in the amplitude of oscillations of the atoms does not always result in a growth in the mean distance between them.

If the oscillations of the atoms were strictly harmonic, then each atom would approach one of its neighbours by the same distance by which it would move away from another one, and an increase in the amplitude of its oscillations would not result in a change in the mean interatomic distance and, therefore, in thermal expansion.

Actually, the atoms in a crystal lattice perform *anharmonic* (i.e. not harmonic) oscillations. This is due to the nature of the dependence of the forces of interaction between atoms on the distance between them. As we pointed out at the beginning of this chapter (see Figs. 152 and 153), this relationship is such that with large interatomic distances the forces of interaction between the atoms manifest themselves as forces of attraction while with reduction of this distance they reverse their sign and become forces of repulsion that rapidly grow with a decreasing distance.

The consequence is that when the "amplitude" of the oscillations of atoms grows owing to heating of a crystal, the growth in the forces of repulsion between the atoms predominates over the growth in the forces of attraction. In other words, an atom finds it "easier" to move away from a neighbour than to approach one. This should naturally result in an increase in the mean distance between atoms, i.e. in an increase in the volume of a body when it is heated.

It thus follows that the cause of thermal expansion of solids is the anharmonic nature of the oscillations of the atoms in a crystal lattice.

Thermal expansion is characterized quantitatively by the coefficients of linear and volume expansion, which are determined as follows. Suppose that a body having the length $l$ changes its length by $\Delta l$ when the temperature is changed by $\Delta T$ kelvins. The coefficient of linear expansion is determined from the relationship

$$\alpha = \frac{1}{l} \frac{\Delta l}{\Delta T} \tag{9.33}$$

i.e. the coefficient of linear expansion equals the relative change in length when the temperature is changed by one kelvin. In exactly the same way, the coefficient of volume expansion $\gamma$ is determined by the expression

$$\gamma = \frac{1}{V} \frac{\Delta V}{\Delta T} \tag{9.34}$$

i.e. the coefficient $\gamma$ equals the relative change in volume $\Delta V/V$ related to one kelvin.

It follows from these equations that the length $l_T$ and the volume $V_T$ at a certain temperature differing from the initial one by $\Delta T$ kelvins are expressed by the relationships (at small values of $\Delta T$):

$$l_T = l_0(1 + \alpha \Delta T) \tag{9.35}$$

and

$$V_T = V_0(1 + \gamma \Delta T) \tag{9.36}$$

where $l_0$ and $V_0$ are the initial length and volume of a body.

Owing to the anisotropy of crystals, the coefficient of linear expansion $\alpha$ may be different in different directions. This means that if we turn a sphere from a given crystal, it will lose its spherical shape after heating. We can show that in the most general case such a sphere when heated transforms into a *general ellipsoid* whose axes are related to the crystallographic axes of the crystal.

The coefficients of thermal expansion along the three axes of this ellipsoid are called the *principal coefficients of expansion* of the crystal.

If we denote them by $\alpha_1$, $\alpha_2$, and $\alpha_3$, respectively, then the coefficient of volume expansion of the crystal is

$$\gamma = \alpha_1 + \alpha_2 + \alpha_3 \tag{9.37}$$

For crystals having cubic symmetry, as for isotropic bodies, we have

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha \quad \text{and} \quad \gamma = 3\alpha$$

A sphere turned from such bodies remains spherical after heating (but naturally has a larger diameter).

In some crystals (for example hexagonal ones), we have $\alpha_1 = \alpha_2$ and $\gamma = 2\alpha_1 + \alpha_3$.

The coefficients of linear and volume expansion remain virtually constant if the temperature intervals within which they are measured are small, and the temperatures themselves are high. In general, however, the coefficients of thermal expansion depend on the temperature, and in the same way as the heat capacity, i.e. at low temperatures the coefficients $\alpha$ and $\gamma$ diminish with lowering of the temperature in proportion to the cube of the latter, tending, like the heat capacity, to zero at absolute zero. This is not surprising because both the heat capacity and thermal expansion are associated with oscillations of the lattice: the heat capacity gives the quantity of heat needed to increase the mean energy of thermal oscillations of the atoms depending on the amplitude of the oscillations; the coefficient of thermal expansion is directly associated with the mean distances between the atoms, which also depend on the amplitude of the atomic oscillations.

Hence follows an important law discovered by E. Grüneisen: *the ratio of the coefficient of thermal expansion to the atomic heat capacity of a*

*solid is a constant quantity for a given substance (i.e. is independent of the temperature).*

The coefficients of thermal expansion of solids are usually very small, as can be seen from Table 22. The values of the coefficient $\alpha$ given in this table relate to the temperature interval between 0 and 100 °C.

*Table 22*

**Coefficients of Thermal Expansion of Selected Solids**

| Substance | $\alpha$, $K^{-1}$ | Substance | $\alpha$, $K^{-1}$ |
|---|---|---|---|
| Aluminium | $26 \times 10^{-6}$ | Phosphorus | $124 \times 10^{-6}$ |
| Brass | $19 \times 10^{-6}$ | Silicon | $7 \times 10^{-6}$ |
| Copper | $17 \times 10^{-6}$ | Silver | $19 \times 10^{-6}$ |
| Duralumin | $22.6 \times 10^{-6}$ | Sodium | $80 \times 10^{-6}$ |
| Iron | $12 \times 10^{-6}$ | Tungsten | $4 \times 10^{-6}$ |
| Molybdenum | $5 \times 10^{-6}$ | Zinc | $28 \times 10^{-6}$ |

Some substances have an especially low coefficient of thermal expansion. This property, for instance, is a feature of quartz ($\alpha = 0.5 \times 10^{-6}$ $K^{-1}$). Another example is the nickel-iron alloy (36% of Ni) known as Invar ($\alpha = 1 \times 10^{-6}$ $K^{-1}$). These substances have come into great favour in precise instrument making.

## 9.22. THERMAL CONDUCTIVITY

If there is a temperature difference between various parts of a solid, then heat will be transferred from the hotter to the colder part, just like what happens in fluids.

Unlike fluids, convection, i.e. the transfer of the mass of a substance together with heat, cannot appear in a solid. Hence, heat is transferred in a solid only by thermal conductivity.

The mechanism of heat transfer in a solid follows from the nature of the thermal movements in it. A solid is a complex of atoms performing oscillations. But these oscillations are not independent of one another. The oscillations can be transferred (with the velocity of sound) from one set of atoms to another, and a wave is formed that transfers the energy of the oscillations. Heat is transferred precisely by such propagation of the oscillations.

The transfer of heat in a solid is described quantitatively in the same way as in a gas. If the quantity of heat $Q$ is transferred through a unit cross-sectional area at right angles to its plane in a unit time, then it is

related with the temperature difference causing this transfer by the equation [see Eq. (3.31)]

$$Q = -\lambda \frac{dT}{dx}$$

where $dT/dx$ is the temperature gradient in the direction $X$. The quantity $Q$ is called the *heat flux*. The value of the thermal conductivity coefficient $\lambda$ cannot be calculated in the same way as for a gas — a simpler system consisting of uninteracting particles.

The thermal conductivity coefficient can be calculated approximately with the aid of quantum notions.

**Phonons.** The quantum theory permits us to compare certain fictitious particles—*phonons*—with oscillations propagating in a solid with the velocity of sound. Each phonon is characterized by an energy equal to the Planck constant, which we already know, multiplied by a quantity called the frequency of oscillations $\nu$ in classical physics. Hence, the energy of a phonon equals $h\nu$.

If we use the notion of phonons, we can say that the thermal movements in a solid are due to them, so that at absolute zero the phonons are absent, while with elevation of the temperature their number grows. This growth, however, is not linear, but follows a more complicated law (at low temperatures it is proportional to the cube of the temperature).

We can now consider a solid as a vessel containing a gas consisting of phonons — a gas which at not very high temperatures can be assumed to be ideal. Like in an ordinary gas, heat is transferred in a phonon gas by collisions of the phonons with atoms of the lattice, and when calculating the thermal conductivity coefficient for ideal gases (see Chap. 3) our reasoning also holds here. Therefore, the thermal conductivity coefficient for a solid can be expressed by absolutely the same equation [see Eq. (3.39)]:

$$\lambda = \frac{1}{3} \rho c_V l c$$

where $\rho$ = density of the solid
$c_V$ = its specific heat capacity
$c$ = velocity of sound in the solid.

It is somewhat more difficult to calculate the free path $l$ of a phonon. An estimation shows that this quantity is inversely proportional to the absolute temperature. Hence, the thermal conductivity coefficient $\lambda$ is also inversely proportional to the temperature:

$$\lambda = \frac{a}{T} \tag{9.38}$$

where $a$ is a constant different for different substances.

In metals, the transfer of heat, apart from the oscillations of the lattice, is also accomplished by charged particles — *electrons*. The latter are also

carriers of an electric current in a metal. At high temperatures, the electronic part of the thermal conductivity is much higher than the lattice part. This explains the high thermal conductivity of metals in comparison with metalloids in which phonons are the only carriers of heat.

Thus, the thermal conductivity coefficient for aluminium is 238 W/m·K whereas for quartz it does not exceed 5. It should be remembered that the thermal conductivity coefficient for gases in standard conditions is about $10^{-3}$ W/m·K. At lower (but not the lowest) temperatures, the lattice thermal conductivity begins to predominate because it grows with lowering of the temperature while the electronic thermal conductivity does not depend on the temperature. At the lowest temperatures, the electronic part of the thermal conductivity again begins to predominate.

In superconductors, however, in which an electric current encounters no resistance, electronic thermal conductivity is virtually absent: the electrons, which carry an electric current with no resistance, do not participate in the transfer of heat, and heat transfer in superconductors is purely of the lattice kind.

**Measurement of Thermal Conductivity.** It can be seen from the thermal conductivity equation (3.31), i.e.

$$Q = -\lambda \frac{dT}{dx}$$

that to determine the thermal conductivity coefficient it is necessary to measure the quantity of heat $Q$ flowing through a unit cross-sectional area of a body in a unit time, and the temperature gradient along the body.

The same difficulties are encountered in such measurements as when measuring the heat capacity. In both cases, we must measure the quantity of heat and the change in temperature. In both cases, part of the supplied quantity of heat may be lost and thus fail to participate in the process being studied. Therefore when measuring the thermal conductivity, like the heat capacity, the main attention must be given to elimination of the error appearing because of the fact that not all of the heat is transferred through the body being studied by thermal conductivity, but may be partly transferred to the surroundings through the side surfaces.

Figure 196 shows a simple arrangement used to measure the thermal conductivity of a solid.

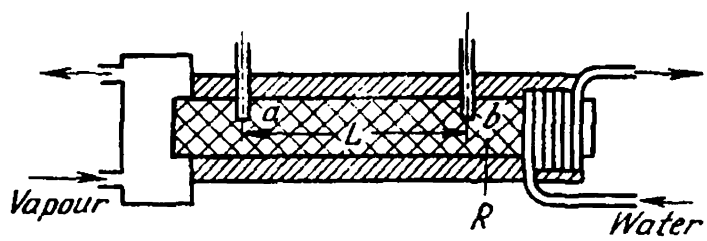



Fig. 196

The substance being studied in the form of rod $R$ is heated at one end by a source of heat (an electric heater, the vapour of a boiling liquid) while its other end is kept at a constant temperature (for example by means of running water). Thermometers or thermocouples are placed at two points of the rod $a$ and $b$ in special depressions.

The rod is surrounded along its entire length by an insulating envelope to reduce the evolution of heat through the side surfaces. It is also good to polish the surface of the rod for the same purpose.

In a certain time after the heater has been switched on, a steady state sets in with an identical temperature gradient along the entire length of the rod. It may therefore be determined as $(T_1 - T_2)/L$, where $T_1$ and $T_2$ are the temperatures at points $a$ and $b$, and $L$ is the distance between these points. The thermal conductivity coefficient is determined from the equation

$$\lambda = \frac{QL}{T_1 - T_2} \tag{9.39}$$

The quantity of heat $Q$ supplied by the heater can easily be determined by measuring the current and the potential difference.

We shall give another example of an arrangement for measuring the thermal conductivity coefficient used for studying substances that conduct heat poorly. In this case, it is more convenient to give the specimen being investigated the shape of a plate or a disk. The arrangement is shown schematically in Fig. 197. Plate $P$ of the substance being studied is placed on massive cooled plate $C$. Heater plate $H$ using an electric current for heating is placed over the specimen.

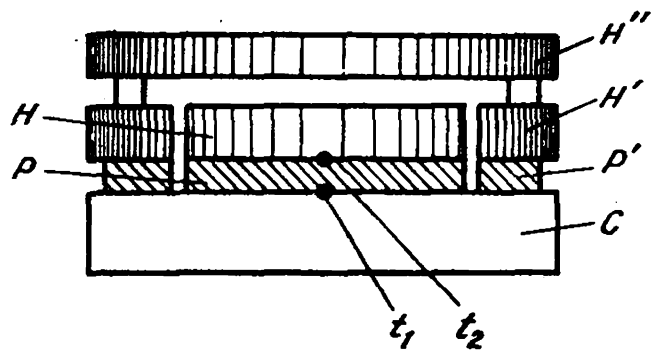



Fig. 197

To eliminate the influence of the edges of the specimen, it is surrounded by ring $P'$ made of the same material. The heater is also surrounded by protective ring $H'$. Finally, another heater $H''$ is placed above heater $H$, and its temperature is kept at such a value that the top and bottom surfaces of main heater $H$ will have the same temperature. This means that the heat passing upward from $H$ is compensated by the heat from $H''$. With such a design of the arrangement, we may consider that the heat from heater $H$ is completely transferred through the specimen being investigated while the specimen itself does not give up heat to the sides because it is protected by a ring heated in the same way as the specimen itself.

Thermometers $t_1$ and $t_2$ measure the temperatures $T_1$ and $T_2$ of both surfaces of the specimen.

From measurements of the quantity of heat $Q$ supplied by the heater and of the temperature difference, the thermal conductivity coefficient is calculated by the expression

$$\lambda = \frac{Qd}{(T_1 - T_2)A} \tag{9.40}$$

where $d$ = thickness of plate $P$
$A$ = its surface area.

The transfer of heat to a side by a specimen can also be eliminated by making the specimen in the form of a hollow cylinder or sphere and placing the heater on the axis of the cylinder or at the centre of the sphere.

## 9.23. DIFFUSION IN SOLIDS

Notwithstanding the fact that a solid is characterized by ordered arrangement of the atoms in a crystal lattice, motion of the atoms is also possible in it. Thermal movements, which mainly have the nature of small oscillations, sometimes result in atoms completely leaving their sites in a lattice. The fact that a solid can evaporate witnesses the possibility of such separation of atoms. True, in evaporation, the atoms separate in the surface layer, but there are no grounds to state that such separation is impossible inside a body.

The appearance of such defects in crystals as Schottky and Frenkel defects is precisely due to the fact that atoms leave their places at lattice points. Diffusion in solids is also associated with these separations of atoms and their following movement in a crystal.

The particles in solids, like those in gases, have different energies of thermal movements. And at any temperature, there is a definite portion of the atoms whose energy considerably exceeds the mean value and is sufficiently great for them to be able to leave their sites in the lattice and pass over to a new position. The higher the temperature, the greater is the number of such atoms. Therefore, the diffusion coefficient $D$ rapidly grows with increasing temperature (according to an exponential law). But since the number of atoms having a sufficiently high energy is always small (if the temperature is much lower than the melting point), then the process of diffusion in a solid is a still slower process than in fluids. For instance, the coefficient of diffusion of copper into gold at 300 °C equals $1.5 \times 10^{-13}$ cm$^2$/s. For comparison, we shall indicate that for the diffusion of an aqueous solution of methyl alcohol into water $D = 1.3 \times 10^{-5}$ cm$^2$/s, and for the diffusion of argon into helium we have $D = 0.7$ cm$^2$/s. Diffusion in solids nevertheless plays a great part in quite a few processes. It is observed both in one-component (in this case we speak of self-diffusion) and in multicomponent substances, in mono- and polycrystals.

Experiments (in particular ones using the so-called tracer atoms) show that diffusion in solids mainly occurs in one of the following three ways.

1. Neighbouring atoms in a lattice exchange places in it as shown in Fig. 198. This exchange, for example, may be a result of turning of the pair of atoms participating in it about their central point.

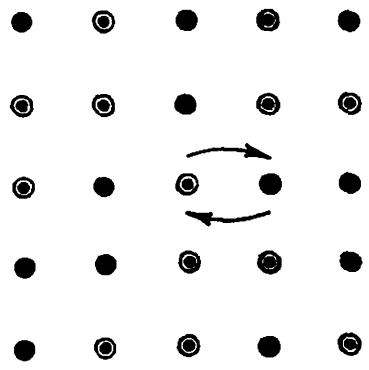


Fig. 198

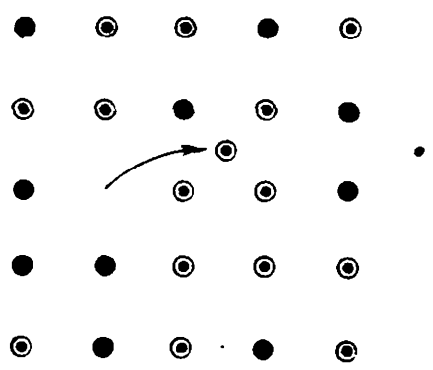


Fig. 199

2. An atom at its "own" place at a lattice point leaves it and takes up a position in an interstice, and then migrates along the interstices (Fig. 199).

3. Atoms from lattice points pass over to unoccupied points, the so-called vacancies (Fig. 200). This process is possible only in defective crystals because vacancies are naturally defects of a crystal. It is clear that the transi-

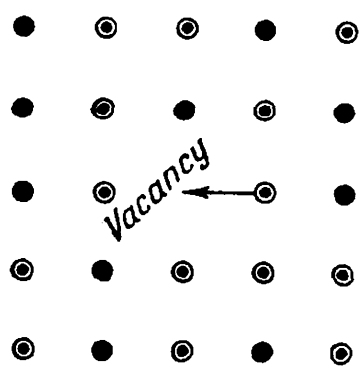



Fig. 200

tion of atoms to vacant sites is equivalent to transition of the vacancies themselves in a direction opposite to that of motion of the atoms.

The most important part is apparently played by the last-named mechanism of diffusion. For it to occur, a gradient of the density of the vacancies must be present in a solid so that the atoms (and, therefore, the vacancies) move more often in one direction than in the other. An important part in polycrystals is played by the process of filling up the vacancies on the boundaries of the crystalline particles (grains). Evidently, dislocations play an important part in the process of creating vacancies without which diffusion is impossible.

In the experimental studying of diffusion in solids, the substances being studied are brought into reliable contact with each other, and are then kept for a long time at the temperature of the experiment. After this, thin layers are consecutively removed at right angles to the direction of diffusion, and the concentrations of the diffused substances are investigated depending on the distance from the place of contact.

Lately, artificial radioactive substances whose presence is easily detected according to their radiation have come into great favour.

This method (the method of tracer atoms) also makes it possible to study the phenomenon of self-diffusion, i.e. the diffusion in a solid of atoms of this solid.

The general law of diffusion in solids is the same as for fluids. This is Fick's law which we have mentioned more than once.

As regards the diffusion coefficient $D$, an expression for it can be obtained from considerations similar to those given on page 314 in connection with the treatment of diffusion in liquids. Diffusion in a solid is also achieved by jumps of the atoms from their positions of equilibrium at the crystal lattice points. But now we can quite definitely say that the length of a jump equals the lattice constant $a$.

It must be remembered, however, that in the vacancy mechanism of diffusion an atom can perform a jump from a lattice point only if the adjacent point is vacant, as shown in Fig. 200. But even with such a neighbour, an atom must have the additional energy $\varepsilon$ for a jump to the vacancy to occur. We know that the potential energy of an atom is minimum at a lattice point. Therefore, any displacement of an atom from a lattice point, including a displacement to an adjacent vacancy, needs additional energy which it can obtain with a certain probability as a result of fluctuation. This probability, as always, is determined by Boltzmann's law

$$\frac{n}{n_0} = \exp\left(-\frac{\varepsilon}{kT}\right)$$

Here $\varepsilon$ is the energy needed for a jump from a lattice point, the *energy of movement of an atom into a vacancy*.

In accordance with considerations given on page 314, the coefficient of self-diffusion in a solid can be written in the form

$$D = \frac{1}{6}\frac{a^2}{\bar{t}} \tag{9.41}$$

where $a$ = lattice constant

$\bar{t}$ = mean time spent by an atom at a lattice point.

The time $\bar{t}$ is obviously the smaller, the greater is the probability of the formation of a vacancy adjacent to an atom and the greater is the probability of an atom receiving the energy of movement $\varepsilon$. We saw on page 315 that the probability of the formation of a vacancy is $\exp\left(-\frac{E_0}{kT}\right)$. Now we

see that the probability of an atom receiving the energy $\varepsilon$ is $\exp\left(-\frac{\varepsilon}{kT}\right)$. Therefore, the expression for the diffusion coefficient can be written in the form

$$D = D_0 \exp\left(-\frac{E_a}{kT}\right) \exp\left(-\frac{\varepsilon}{kT}\right) = D_0 \exp\left(-\frac{E_a + \varepsilon}{kT}\right) =$$

$$= D_0 \exp\left(-\frac{E_{ad}}{kT}\right) \tag{9.42}$$

The factor $D_0$ (the so-called preexponential factor) is a constant characteristic of a given substance. The quantity $E_{ad}$ equal to the sum of the energy of formation of a vacancy $E_a$ and the energy $\varepsilon$ of movement of an atom into the vacancy is called the *diffusion activation energy* and is also a quantity characteristic of a given substance.

The diffusion coefficient has a very small value for solids. For gold, for example, at room temperature it is of the order of magnitude of $10^{-35}$. Even near the melting point of gold, it reaches a value of only $10^{-9}$ cm$^2$/s. These two figures show, however, how greatly the diffusion coefficient depends on the temperature.

The small value of the diffusion coefficient for solids is explained by the fact that for a diffusion jump of an atom into a vacancy to occur, generally speaking, two events with low probabilities must take place virtually at the same time: a vacancy must be formed next to an atom, and as a result of fluctuation the atom itself must receive the energy needed for the jump.

With other diffusion mechanisms, when some substances diffuse into others, the coefficient of diffusion is calculated in a different way. The reader will learn about this from special courses. But in all cases, the diffusion coefficients are small in absolute value. For instance, the coefficient of diffusion of sulphur into iron even at a temperature close to 1000 °C is approximately $2.7 \times 10^{-13}$ m$^2$/s or $2.7 \times 10^{-9}$ cm$^2$/s. But notwithstanding the small values of the diffusion coefficients for solids, the part played by diffusion in them is very great. It is diffusion that ensures such phenomena and processes in solids as annealing for eliminating heterogeneities in alloys, saturation of the surfaces of machine components with carbon, nitrogen, etc., the sintering of powders, and other metal-working processes.

# APPENDICES

*Appendix 1*

## List of Symbols

$A$ area*; constant; free energy; function
$a$ constant; lattice constant; radius of a particle; van der Waals constant
$B$ constant
$b$ van der Waals constant
$C$ constant; integration constant; number of combinations; proportionality factor
$c$ concentration; velocity of sound
$D$ diffusion coefficient
$D_0$ preexponential factor
$d$ diameter; distance; thickness
$E$ energy; mechanical equivalent of heat; Young's modulus (modulus of elasticity)
$E'$ thermal equivalent of mechanical work
$e$ base of natural logarithms; charge of electron
$F$ force
$f$ force of friction; surface force
$G$ arbitrary quantity; shear modulus; weight
$g$ acceleration of free fall
grad gradient
$H$ enthalpy; height
$h$ height; Planck constant
$I$ current intensity; diffusion flux; integration constant
$i$ ionic current intensity; number of degrees of freedom
$K$ compressibility coefficient; factor; partition coefficient
$k$ Boltzmann constant; Henry's coefficient
$L$ heat of transformation; length
$l$ length; mean free path
$M$ bulk modulus; mass; water equivalent of calorimeter
$M'$ modulus of lateral compression in longitudinal tension
$m$ exponent; mass; mass of molecule; molality
$N$ diffusion flux; number of molecules or particles
$N_A$ Avogadro constant
$n$ number of molecules or moles; velocity of rotational motion
$P$ force (weight); power; probability
$p$ pressure
$\bar{p}$ momentum

---

* The symbol $A_s$ is used when necessary to avoid confusion.

$Q$ heat flux; quantity of gas; quantity of heat
$q$ separation factor
$R$ molar gas constant; radius
$Re$ Reynold's number
$r$ distance between atoms; radius; ratio
$S$ entropy
$T$ absolute temperature
$t$ temperature, °C; time
$U$ internal energy; potential difference
$u$ relative velocity; velocity
$V$ volume
$v$ velocity
$W$ thermodynamic probability; work
$w$ concentration (mass fraction) of substance
$x$ mole fraction of substance
$Z$ atomic number; number of collisions
$z$ variable
$z'$ number of collisions along unit length
$\alpha$ coefficient of linear expansion; coefficient of extension; cubic expansion coefficient of gas at constant pressure; thermodiffusion constant
$\beta$ refrigerating factor
$\gamma$ coefficient of volume expansion; ratio of heat capacities $C_p/C_V$
$\Delta$ logarithmic decrement
$\delta$ distance
$\varepsilon$ energy of movement of an atom to a vacancy; strain
$\eta$ coefficient of internal friction (viscosity); efficiency
$\Theta$ Debye characteristic temperature
$\theta$ contact angle
$\varkappa$ compressibility
$\lambda$ thermal conductivity coefficient; wavelength
$\mu$ molecular mass; Poisson's ratio; relative mass
$\mu_J$ Joule-Thomson coefficient
$\nu$ frequency
$\pi$ osmotic pressure; ratio of circumference to diameter of circle, 3.141 59; reduced pressure
$\rho$ density
$\Sigma$ sum
$\sigma$ area of cross section; normal stress; surface tension
$\tau$ reduced temperature; shear stress
$\psi$ angle; angle of shear
$\Omega$ volume
$\omega$ reduced volume; volume

## Conversion Factors for Converting SI Units to Units of Other Systems and Non-System Units

| Quantity | Units and Their Conversion Factors | |
|---|---|---|
| Force | 1 dyn | $= 10^{-5}$ N |
| | | $= 1.02\times10^{-6}$ kgf |
| | 1 kgf | = 9.806 65 N |
| | | $= 9.80\times10^{5}$ dyn |
| | 1 N | $= 10^{5}$ dyn |
| | | = 0.102 kgf |
| Work, energy, quantity of heat | 1 erg | $= 10^{-7}$ J |
| | | $= 1.02\times10^{-8}$ kg·m |
| | | $= 2.39\times10^{-8}$ cal |
| | 1 J | $= 10^{7}$ erg |
| | | = 0.239 cal |
| | | = 0.102 kg·m |
| | 1 cal | = 4.1868 J |
| | | $= 4.1868\times10^{7}$ erg |
| | | = 0.427 kg·m |
| | 1 kg·m | = 9.806 65 J |
| | | $= 9.806\,65\times10^{7}$ erg |
| | | = 2.34 cal |
| Pressure | 1 N/m² (Pa) | = 10 dyn/cm² |
| | | $= 10^{-5}$ bar |
| | | $= 9.87\times10^{-6}$ atm |
| | | $= 7.52\times10^{-3}$ torr |
| | 1 atm | $= 1.013\times10^{5}$ Pa |
| | | $= 1.013\times10^{6}$ dyn/cm² |
| | | = 1.013 bar |
| | | = 760 torr |

| Quantity | Units and Their Conversion Factors |
|---|---|
| Pressure | 1 torr (mm Hg) $= 1.31\times10^{-3}$ atm |
| | $= 1.33\times10^{-3}$ bar |
| | $= 1.33\times10^{2}$ Pa |
| | $= 1.33\times10^{3}$ dyn/cm$^2$ |
| | 1 bar $= 10^{5}$ Pa |
| | $= 10^{6}$ dyn/cm$^2$ |
| | $= 0.987$ atm |
| | $= 750.24$ torr |
| | 1 dyn/cm$^2$ $= 0.1$ Pa |
| | $= 10^{-6}$ bar |
| | $= 9.87\times10^{-7}$ atm |
| | $= 7.52\times10^{-4}$ torr |
| Specific heat capacity | 1 J/kg·K $= 2.39\times10^{-4}$ cal/g·K |
| | 1 cal/g·K $= 4.1868\times10^{3}$ J/kg·K |
| Molar heat capacity | 1 J/mol·K $= 0.239$ cal/mol·K |
| | 1 cal/mol·K $= 4.1868$ J/mol·K |
| Viscosity (coefficient of internal friction) | 1 N·s/m$^2$ $= 10$ P (dyn·s/cm$^2$) |
| | 1 P (dyn·s/cm$^2$) $= 0.1$ N·s/m$^2$ |
| Coefficient of thermal conductivity | 1 W/m·K $= 2.39\times10^{-3}$ cal/cm·s·K |
| | 1 cal/cm·s·K $= 418.68$ W/m·K |
| Diffusion coefficient | 1 m$^2$/s $= 10^{4}$ cm$^2$/s |
| | 1 cm$^2$/s $= 10^{-4}$ m$^2$/s |
| Surface tension | 1 N/m (J/m$^2$) $= 10^{3}$ dyn/cm (erg/cm$^2$) |
| | 1 dyn/cm (erg/cm$^2$) $= 10^{-3}$ N/m |
| Specific heat | 1 J/kg $= 2.39\times10^{-4}$ cal/g |
| | 1 cal/g $= 4186.8$ J/kg |

# NAME INDEX


Andrews, T., 214

Bernoulli, D., 22
Boltzmann L., 64, 74, 111, 288, 289
Borman, E., 143, 145
Born, M., 143, 145
Brown, R., 43

Cagniard de la Tour, C., 364
Carnot, S., 258
Claude, G., 375, 376
Clausius, R., 269
Collins, S. C., 376
Curie, P., 435

Debye, P. J., 453
Dulong, P. L., 310

Easterman, J., 84, 86
Einstein, A., 45, 451, 453

Fedorov, E. S., 403
Franck, J., 425

Gadolin, A. V., 400
Gay-Lussac, J. L., 38
Grüneisen, E., 457

Hampson, W., 372
Henry, W., 360

Joffe, A. F., 417, 424
Joly, P., 129
Joule, J. P., 99, 127, 364, 369

Kapitza, P. L., 376, 383, 391
Kikoin, A. K., 387
Kurnakov, N. S., 444

Landau, L. D., 385
Laplace, P. S., 59
Lazarev, B. G., 387
Linde, P. K. G., von, 372
Lorentz, H. A., 269
Loschmidt, J., 156

Maxwell, J. C., 64, 74, 229, 294
Mendeleev, D. I., 15

Nernst, W. H., 297

Perrin, J., 49, 50, 54, 55, 56
Petit, A. T., 310
Plateau, J., 323

Raoult, F. M., 359
Read, W. T., 425
Regnault, H. V., 130, 310
Reynolds, O., 196

Schleiermacher, H., 170
Simpson, O. C., 84, 86
Smoluchowski, M., 45
Sommerfeld, A., 115
Stern, O., 42, 43, 84, 86

Thomson, W. (Kelvin), 255, 297, 364, 369

Van der Waals, J. D., 221
Van't Hoff, J. H., 362

Young, T., 409

# SUBJECT INDEX


Acceleration, gravity, and altitude, 53
Additivity, definition, 28
Adiabat, ideal gas, 121
Aftereffect, elastic, 416f
Air, liquefaction, 376
Alloys, 441ff
Angles, contact, 326ff
Anisotropy, 395
Annealing, 419
Area, cross-sectional, effective, 135f
Argon, constants of van der Waals equation, 235
Atmosphere(s),
  physical, 26
  planets', 83
  technical, 26
Atom(s),
  distribution by velocities, 43
  energy levels, 18f
  forces of interaction, 394
  ionization, 16
  mass, 16
  mean square velocity, 43
  "mechanized" model, 15

Bar, 25
Barn, 142
Barometers, 88f
Beams, molecular, 42
  scattering in gas, 142f
Bending, 410
Body(ies), *see also* Substance(s)
  crystalline, 393
  working, 255
    changes in state in Carnot cycle, 268ff
Boiling, 351ff
  and altitude, 353
  point,
    and external pressure, 353
    solutions, 360f

Calorie, 99
  fifteen-degree, 128
  international thermal, 128
  thermochemical, 128
  twenty-degree, 128
Calorimeters, 128f, 454f
  heat equivalent, 128
  water equivalent, 128
Capillary(ies), 332
  phenomena, 332ff
  rise, 332ff
    negative, 333
  waves, 336
Carbon, phase diagram, 432f
Carbon dioxide, equation of state, 214f
Cell, elementary, 397
Chamber,
  bubble, 355f
  Wilson cloud, 350f
Coefficient(s),
  compressibility, 412
  cubic expansion, 38, 306
    and compressibility, 307ff
    experimental determination, 309ff
  diffusion, 47, 153, 194
    measurement, 156f
    in solid, 464f
    and temperature, 462
    and viscosity, 179
  extension, 411
  interdiffusion, 154ff
  Joule-Thomson, 365ff
    ideal gas, 367
    real gases, 368f
  linear expansion, 456ff
  partition, 446
  performance, 370f
  self-diffusion, 153, 194
    liquids, 314f
    solids, 464
  shear, 413
  temperature conductivity, 165, 179f
  temperature diffusion, 180
  temperature resistance, 94
  thermal conductivity, 162, 167f, 176, 459f
    measurement, 169ff
    and molecule size, 168f
    and pressure, 167f, 183
    and temperature, 167f
    and viscosity, 176
  thermal diffusion, 158
  thermal expansion,
    and atomic heat capacity, 457f
    and temperature, 457
  velocity diffusion, *see* Viscosity, kinematic
  virial, 236, 381
  volume expansion, 456

Collisions,
molecules, 21, 131, 133ff
probability, 140ff
Column, separating, 160
Compressibility,
and cubic expansion coefficient, 370ff
at critical point, 233
ideal gas, 37, 126
isothermal, 37f
liquids, 304ff
Compression, 409
uniaxial, 410f
uniform (bulk), 412
Concentration, 356f
mass, 356
molar, 356
relative, 155
Condensation, 211f, 340, 341
centres, 350
latent heat, 341
Conductivity, thermal, 133, 161ff, 458ff
liquid helium II, 390f
liquids, 316
measurement, 460ff
non-stationary, 162ff
stationary, 165ff
Constant(s),
Avogadro, 35
determination, 50
Boltzmann, 33
determination, 43, 49f, 52, 55f
crystal lattice, 403
gravitational, 53
molar gas, 36, 107
Planck, 451
thermodiffusion, 158f
time, thermal conductivity, 165
van der Waals equation, 226
argon, 235
calculation, 222ff
experimental determination, 233f
and temperature, 235
Convection, 169f
Cooling, magnetic method, 378f
Counterpressure, 198
Cryostat, 377f
Crystal(s),
cleavage plane, 396
slipping along, 420
defects, 405ff
equilibrium concentration, 407f
Frenkel, 406
linear, 407
point, 406
Schottky, 406
surface, 407
volume, 407
Crystal(s),
dislocations, *see* Dislocations
elementary cell, 397
lattice, *see* Crystal lattice
Miller indices, 404
directions, 404f
planes, 404
slipping in, 420f
symbols for planes and directions, 403ff
symmetry, *see* Symmetry of crystals
translation, *see* Translation
Crystal lattice, 395ff
Bravais, 401ff
face-centered, 401
number of kinds, 402
volume-centered, 401
constants, 403
geometry, 396f
points, 401
space, 397
space group, 403
vacancy, 408
Crystallization, 427f
from solution, 440
Curve(s),
phase equilibrium, 219
stress-strain, 417ff
sublimation, 430f, 432
vaporization, 430f, 432
Cycle,
Carnot, 256ff, 345f
efficiency, 261f
inverted, 262
refrigerating, 262
work, 258ff
definition, 254

Defects, crystals, 405ff
Deformation, 408, *see also* Strain(s)
plastic, 417ff
mechanism, 420ff
Degree, value, 28f
Density,
critical, determination, 221
gas, 41
probability, 64
saturated water vapour, and temperature, 213
steam, and temperature, 213
and temperature, 215
water, and temperature, 213
Diagrams,
fusibility, 441ff
phase, 218f, 430ff 441ff
carbon, 432f
helium, 437

Diagrams,
property-composition, 444
Diamonds, artificial, production, 433
Diffusion,
activation energy, 465
coefficient, 147, 153, 194
flux, 145ff, 152
forced, 160
gas, 133, 145ff
in vacuum, 194f
in solids, 462ff
steady-state, 146, 151ff
thermal, 157ff
coefficient, 158
unsteady-state, 146, 148ff, 194
Dilatometer, 309f
Dislocations, 406f, 422ff
edge, 423
and heat treatment, 425f
and impurities, 425
and strain hardening, 424f
Dissociation, 13
Dissolution, 439
and cooling, 439
mechanism, 357
Distribution, Maxwell-Boltzmann, 75

Ebullioscopy, 361
Effect,
fountain, 388
Joffe, 424
Joule-Thomson, 305ff
mechanocaloric, 389f
Seebeck, 94f
thermomechanical, in liquid helium II, 387ff
Efficiency,
Carnot cycle, 261f
heat engine, 261, 263, 283
irreversible cycle, 264
refrigerating machine, 370
reversible Carnot machine, 264
ways of improvement, 265
Effusion,
gas, 187
molecular, 187
Electron(s), 459
charge, 15
Elongation, unit, 410
Energy,
activation,
diffusion, 465
molecule, 315
bound, 287
free, 266ff
gas particle motion, 33
Energy,
internal, 97f, 102
ideal gas, 267
and volume, 276ff
kinetic, mean, 25, 31f
levels in atom, 18f
mechanical, conversion to heat, 251
molecule, mean, 97, 166, 451f
vibrational degree of freedom, 113
zero, 438f, 449
Enthalpy, 108f, 366
ideal monatomic gas, 109
Entropy, 269ff
closed system,
irreversible process, 279ff
reversible process, 278
and disorder, 293
and energy of system, 301
expressions for, 273ff
increase,
in adiabatic expansion of ideal gas into a vacuum, 282
in heat transfer, 281f
influence on availability of heat for conversion to work, 287
in interdiffusion of gases, 282f
main properties, 293
maximum value, 281
and probability, 288ff
Equation,
adiabat, 121
Boltzmann, 57
Clapeyron-Clausius, 346f
Clapeyron-Mendeleev, 36
Frenkel-Andrade, 315f
fundamental, kinetic theory of gases, 25
isobar, 38
isotherm, 37
Laplace, 330
law of conservation of energy, 106
Maxwell, for relative velocities, 80
Poiseuille, 317
Poisson, 121
polytrope, 125
state, 34f
carbon dioxide, for high pressures, 214f
ideal gases, 35f
real gas, 25
general, 236
reduced, 237
van der Waals, 221ff
comparison with experimental data, 234ff
constants, 222ff, 226, 233ff
deviations from, 235
reduced, 237

Equilibrium,
on interface between two media, 325f
liquid-solid interface, 327ff
liquid-vapour, 339f
phase, 216, 218
statistical, 242ff
thermal, 27, 30
thermodynamic, 242ff
Eutectic, 442
Evaporation, 340
Expander, gas, 371, 375f
Experiment(s),
Perrin's, 49f, 54ff
Plateau, 322f
Stern's, 42f
Exponent,
adiabatic, 121
polytropic, 125f

Factor,
enrichment, 159f, 190f
refrigerating, 370f
scattering, 143
separation, 159
Films, thin, in liquid helium II, 386f
Flow,
Knudsen, 187
laminar, 177
molecular, 184ff
in cylindrical tube, 187ff
gas mixture, 189ff
isotope separation, 192
turbulent, 177f
Fluctuations, 44, 244, 292, 351f, 354, 435f
Flux,
diffusion, 145ff, 152
heat, 162, 459
Force(s),
attraction between molecules, 224ff
cohesion between wetted plates, 335
on curved liquid surface, 329ff
elastic, 409
intermolecular, 12
nuclear, 17
repulsion between molecules, 222
Formula,
barometric, 52
Poiseuille, 173
Stokes, 45
Fraction,
mass, 356
mole, 356
Friction, internal, *see* Viscosity
Function, distribution, 63ff

Gas(es), *see also* Vapour
compressibility, and pressure, 209
condensation, 211f
cooling, in adiabatic expansion, 370
cubic expansion coefficient, 38
density, 41, 187
deviation of properties from ideal gas laws, 208ff
diffusion, 133, 145ff
in vacuum, 194f
effusion, 187
expander, 371, 375f
expansion into vacuum, 126f, 282
flow at low pressures, *see* Flow, molecular
heat capacity, 106ff, 110f, 113, 176, 239f
heat transfer at low pressures, 182ff
ideal, 20ff
compressibility, 37f
adiabatic, 126
definition, 21
enthalpy, 109
equation of state, 35f
internal energy, 97f, 102
isothermal expansion, 253
isotherms, 37, 121
temperature scale, 29
internal energy, 267
internal friction, 133, *see also* Viscosity
liquefaction, *see* Liquefaction
liquefied, properties, 376ff
at low temperatures, 380ff
mixtures, separation, 189ff
molecule velocity, *see* Molecule(s), velocity
parameters in adiabatic process, 121f
pressure, 21ff
and temperature, 225
real,
equation of state, 225
forces of molecular interaction, 237f
internal energy, 239
sorption, 202
thermal conductivity, 133, 161ff
thermal transpiration, 196f
throttling, 365
viscosity, 133, 171ff
calculations, 174ff
Gauges, pressure 87ff
Bourdon, 89
differential, 88
piston, 89f
Getters, 202
Gradient, definition, 146

Hardening, 419
  work, 419
Heat,
  capacity, *see* Heat capacity
  content, *see* Enthalpy
  conversion to mechanical energy, 251
  conversion to mechanical work, 253ff, 283ff
  definition, 253
  engine, 262
  exchange, counterflow, 372
  exchanger, 373
  flux, 162
  function, 366
  latent,
    condensation, 341
    fusion, 427
      determination, 448
      specific, 429
    solidification, 426
    vaporization, 340ff
  mechanical equivalent, 99
  quantity, 99
    measurement, 128
    units, 127f
  reduced, 269
  solution, 357f
    specific, 439
  sublimation, 430
  transfer in low-pressure gases, 182ff
Heat capacity, 105
  atomic, 449f
  at constant pressure, 106ff, 240
    measurement, 130f
    and temperature, 450, 452
  at constant volume, 106ff, 240
    measurement, 129
    solids, 416, 449ff
  gases, 176
    diatomic, 110f
    monatomic, 106ff
    polyatomic, 110f, 113
    real, 239f
  hydrogen, 115ff
  liquids, 312f
  measurement, 128ff, 453ff
    ratio $C_p/C_V$, 131
    Regnault's method, 130
  molar, 105ff, 450
  number of degrees of freedom, 109f
  specific, 105, 176
  and temperature, 115ff
Heater, 255
Helium,
  liquefaction, 376
  liquid, 382ff
Helium,
  liquid,
    modifications, 383
    rate of flow (He II), 384
    thermal conductivity (He II), 390f
  phase diagram, 437
  solid, 437ff
Hypsothermometer, 353

Identity, thermodynamic, 272, 276
Indices, Miller, 404f
Inequality, Clausius, 273
Irreversibility, and probability, 250
Isotherm(s),
  critical, 215f
  experimental, 227
  ideal gas, 37, 121
  van der Waals, 226ff
Isotopes, 17
  separation, 192

Joule, 99

Kelvin, 30, 34, 297
Kilocalorie, 99

Lattice, crystal, *see* Crystal lattice
Law(s),
  Avogadro, 39
  Boltzmann, 57, 60, 343
  Boyle's, 37
  Charle's, 38
  conservation of energy, 65, 100, 251f, 287
    adiabatic process, 119
    equation, 106
  corresponding states, 237, 381
  Dalton's, 39f
  Dulong and Petit, 450f
    deviations from, 450f, 453
  equipartition, 111f
  Fick's, 146f
  Fourier, 162
  Gay-Lussac, 38
  Grüneisen's, 457f
  Henry's, 359f
  Hooke's, 409, 410, 412, 413, 422
  Maxwell distribution, 71
    experimental verification, 84ff
  physical application limits, 208
  Poiseuille, application, 188
  quantum mechanics, 17f
  Raoult's, 359f
    deviations from, 359

Law(s),
thermodynamics,
first, 100, 127, 251ff
second, 281, 284ff, 291f
reversible processes, 272
third, 297f
van't Hoff, 362
Levelling, zone, 447
Limit, elastic, 417
Line,
liquidus, 443
solidus, 443
Liquefaction, 210ff, 363f, 372
by adiabatic expansion, 375f
air, 376
Claude process, 375f
helium, 376
Linde method, 372ff
using Joule-Thomson effect, 372ff
Liquid(s),
boiling, *see* Boiling
compressibility, 304ff
experimental determination, 305f
and pressure, 304f
and temperature, 305
diffusion in, 314
drops, 323f
equilibrium with vapour, 339f
forces on curved surface, 329ff
heat capacity, 312f
and temperature, 313
interface with solid, 327ff
at low temperatures, 382
main features, 303
non-wetting, 328
pressures of curved surfaces on, 329ff
rate of flow, 384
critical, 384
self-diffusion coefficient, 314f
superheated, 228
superheating, 353ff
and hydrostatic pressure, 355
prevention, 354
surface tension, *see* Surface tension
thermal conductivity, 316
thermal expansion, 306f
viscosity, 315f
experimental determination, 316f
wetting, 328

Machine,
Linde, 372ff
perpetual motion, 284f
refrigerating, 262
efficiency, 370

Manometer,
ionization, 203f
liquid, 88f
McLeod, 205f
shortcomings, 206
thermo-conduction, 204f
Maxwell "demon", 294
Melting, 431f
Membrane, semipermeable, 361
Meniscus, 328
Metals,
pure, properties, 419
zone purification, 445ff
Method,
capillary wave, 336
cryoscopic, 441
drop and bubble, 336ff
magnetic cooling, 378f
oscillation damping, 178f
surface ionization, 85
Mixtures, gas, separation, 189ff
Modulus,
bulk, 412
elasticity, 410
and bulk modulus, 414
and shear modulus, 413ff
lateral compression in longitudinal tension, 411
shear, 413, 415, 422
Young's, 410f, 415
Molality, 356
Mole, 35
Molecule(s),
activation energy, 315
collisions, 21, 131, 133ff
mean number, 136ff
cross section, effective, 140ff
definition, 13
density and altitude, 64
distribution by velocities, 43, 62f, 70ff
and temperature, 74
distribution by velocity components, 65ff
energy, mean, 97, 166
forces,
attraction, 224ff, 238
interaction in real gas, 237f
repulsion, 222, 238
free path, 136
experimental determination, 143ff
mean, 136, 138
and pressure, 139, 181f
and temperature, 139f
number of degrees of freedom, 110, 112ff
potential energy, 57
random motion, 75
scattering, 134

Molecule(s),
velocity, 132
arithmetic mean, 75ff
effective, 25, 41, 61f, 78
experimental determination, 41ff
Maxwell distribution law, 71
mean square, 25, 41, 61f, 78
most probable, 72, 78f
Monocrystal, preparation, 428, 440
Motion, thermal, 13
Movement, Brownian, 43ff

Neutron, 16
Nitrogen, density and temperature, 215
Non-wetting,
complete, 328
partial, 328
Nucleons, 16
Number,
degrees of freedom,
diatomic molecule, 112
gas molecules, 110, 112ff
polyatomic molecule, 112f
Loschmidt, 39
Reynolds, 177

Orbit, permissible, 18
Order,
long-range, 393
short-range, 393
Orthohydrogen, 116f
Osmosis, 362

Parahydrogen, 116f
Parameters,
critical, 215f
determination, 219f
reduced, 236
state, solids, 393
Pascal, 25
Phase,
definition, 216
equilibrium, 216, 218
transition, 216
Phenomena, capillary
Phonon, 453, 459f
Piezometer, 305f
Plane, cleavage, 396
slipping along, 420
Point,
boiling,
and external pressure, 353
solutions, 360f
Curie, 435
eutectic, 442

Point,
freezing, 426
and pressure, 428
solution, 439, 440
lambda, 383, 435
melting,
experimental determination, 447f
and pressure, 428
solidification, *see* Point, freezing
triple, 413f
water, 34
yield, 417
Poise, 173
Polymorphism, 432
Press, Cailletet, 211f
Pressure,
air, and altitude, 52f
barometric, determination, 353
critical, 215f, 230ff
gauges, *see* Barometers; Gauges, pressure; Manometer
hydrostatic, and superheating, 355
measurement, 87, 202ff
osmotic, 362
partial, 40
reduced, 236
saturated vapour, 340
and altitude, 348
over curved liquid surface, 347ff
over ideal solution, 358f
over solid, 430
and temperature, 218f, 343ff
units, 25f
Principle,
Carnot's, 255
Kelvin's, 255
unattainability of absolute zero, 298
Probability(ies), 57ff
density, 64
and mean values of quantities, 60f
multiplication, 60
particle distribution, 289
summation, 59
thermodynamic, 289ff
and entropy, 289ff
Process,
adiabatic, 118f, 121
relationship between gas parameters, 121f
work, 119f, 122f, 259, 265
cross section, 135
cyclic, 102f, 252, 254ff
irreversible, 244, 245f
entropy, 279ff
isochoric, 38f
isothermal, 117f
reversible, 266

Process,
isothermal,
work, 118f, 123f, 258f, 266
non-stationary, 146
polytropic, 124ff
quasistatic, 103f, 246f, 250
reversible, 244f, 247
stationary, 146
thermal, irreversibility, 293
time constant, 150
zone-melting, 445ff
zone-vacuum, 447
Proton, 16
number in nucleus, 16f
Pumps, 198ff
diffusion, 200ff
fore, 198ff
high-vacuum, 200
rotary oil, 198f
vacuum, 198f
vapour-jet, 200ff

Quantity,
mean value, 61
thermometric, 28f
Quenching, 419

Raindrops, formation, 349f
Ratio, Poisson's, 411f, 415
Relaxation, 244
Reservoir,
cold, 255
hot, 255
Rise, capillary, 332ff
negative, 333

Scale, temperature, 29
absolute, 30
Celsius, 30
ideal gas, 29
International practical, 92
Kelvin, 30
thermodynamic, 295f
Sections, cross, gas-kinetic, 180
Self-diffusion, 153
coefficient, 153, 194, 314f, 464
Set, permanent, 417
Shear, 410, 412f
Sink, heat, 255
Solid(s),
diffusion, 462ff
features, 399
heat capacity, 449
at constant volume, 416, 449ff
Solid(s),
relationship between parameters of state, 393
spectrum of oscillations, 453
thermal expansion, 455ff
thermal motion in, 448f
Solubility, 357, 440
Solute, 356
Solution(s),
boiling point, 360f
definition, 356
heat, 357f
ideal, 358
liquid, 356ff
real, deviations from Raoult's law, 359
saturated, 357, 440
solid, 441f
Solvent, 356
Source, heat, 255
State(s),
critical, 215
equation, 34f
ideal gases, 35f
real gases, 225
equilibrium, 61, 75, 242ff
metastable, 228
parameters, 34
solids, 393
probability, 249f, 288
unstable, 227f
Stokes, 173
Strain, 408ff, *see also* Deformation
elastic, 408f
permanent, 417
plastic, 408
static, 409
Strength, ultimate, 418
Stress, 409
shearing, 420ff
thermal, 307
Sublimation, 429f
Substance(s),
amorphous, 399
brittle, 418
idea of molecular structure, 12
properties at low temperatures, 380ff
thermometric, 28f
working, *see* Body(ies), working
Superfluidity, helium II, 383ff
Surface, curved, pressure on liquid, 329ff
Surface tension, 318ff
determination, 323f
forces, 320ff
influence of second medium, 324f
measurement, 335ff
capillary wave method, 336
drop and bubble method, 336ff

Surface tension,
and temperature, 339
Symmetry of crystals, 397ff
axis, 398f
centre, 399
classes, 400
elements, 398f
glide-reflection plane, 401
screw axis, 401
plane, 398, 399
rotoflection axis, 399
systems, 400
System,
closed, 278
vacuum, 206f

Table, periodic, 15f
Temperature, 26ff
absolute, 30
absolute zero, unattainability, 297
critical, 213f, 216, 230ff
Debye characteristic, 453
extremely low, 378ff
high, measurement, 95f
inversion, 368f
and critical temperature, 369
and kinetic energy, 32
liquid-helium, 380
low, measurement, 96
measurement, 28, 90ff
negative, 33, 298ff
reduced, 236
units, 28ff
Tempering, 419
Tension, 409
surface, *see* Surface tension
uniaxial, 410f
uniform, 412
Theorem,
Carnot's,
first, 261, 263
second, 261, 263f
Nernst's, 297
Theory, superfluidity, Landau's, 385f
Thermistors, 94
Thermocouples, 94f
Thermodiffusion, 157ff
Thermodynamics, definition, 242
Thermometers, 28
gas, 29f, 90ff
liquid-filled, 92f
mercury, 93
resistance, 93
secondary, 92ff
Time, relaxation, 244, 247, 417
Torr, 26
Torsion, 410
Transition,
graphite-diamond, 433
heat, 341, *see also* Heat, latent
liquid-solid, 426ff
phase, 216
first kind (first-order), 353, 434f
second kind (second-order), 434ff
polymorphic, 432f
solid-gas, 429
to solid state, 426ff
vapour-liquid, 216ff
Translation, 396
group, 397
period, 396
Transpiration, thermal, 196f

Units, SI, 34

Vacancy, 408
Vacuum, 181
Vaporization, 340
and gas bubbles, 352
latent heat, 340f
measurement, 341f, 344
and temperature, 342f
Vapour, *see also* Gas(es)
equilibrium with liquid, 339f
saturated, 212f, 339
pressure, *see* Pressure, saturated vapour
supercooled, 228
supersaturated, 228, 350
Velocity,
atoms, effective, 43
component, arithmetic mean value, 77
escape, 83
molecules, *see* Molecule(s), velocity
reduced, 149
relative, 79
Maxwell equation, 80
second-cosmic, 83
Vessels,
capillary, 332
Dewar, 183f
Viscosimeters, 316f
capillary, 177, 317
Viscosity,
and coefficient of thermal conductivity, 176
definition, 173
and diffusion coefficient, 179
dynamic, 173
gas, 133, 171ff
calculations, 174ff

Viscosity,
kinematic, 173, 179
liquids, 315f
experimental determination, 316f
measurement, 177
method of oscillation damping, 178f
and temperature, 176, 316
Volume,
critical, calculation, 230f
measurement, 86
reduced, 236
Volumeter, 87

Water, anomaly, 312
Waves, capillary, 336
Wetting,
complete, 328
partial, 328
Work,
adiabatic process, 119f, 122f, 259, 265
Carnot cycle, 258ff
in changing gas volume, 100ff
external, 102
isothermal process, 118f, 123f, 258f, 266
comparison with adiabatic process, 123f
negative, 259
positive, 258f
thermal equivalent, 99

Zero, absolute, 30, 33

*Printed in Romania*